

1990

Burial Diagenesis of the Smackover Formation, Southeast Mississippi Salt Basin.

E Heydari-l.

Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation

Heydari-l., E, "Burial Diagenesis of the Smackover Formation, Southeast Mississippi Salt Basin." (1990). *LSU Historical Dissertations and Theses*. 4920.

https://digitalcommons.lsu.edu/gradschool_disstheses/4920

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Order Number 9104138

**Burial diagenesis of the Smackover Formation, southeast
Mississippi salt basin**

Heydari-L., E., Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1990

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

BURIAL DIAGENESIS OF THE SMACKOVER FORMATION,
SOUTHEAST MISSISSIPPI SALT BASIN

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Geology and Geophysics

by

E. Heydari-L.

B.S., University of Tehran, 1976

M.S., The Pennsylvania State University, 1981

May, 1990

ACKNOWLEDGEMENT

Thanks to my dissertation advisor Dr. C. H. Moore for his patience and constant constructive criticism of this research. I also thank the members of the dissertation committee: Drs. P. Aharon, J. S. Hanor, D. Henry, G. Herman, and D. Nummedal. I appreciate Shell, Sun, Phillips, and Texaco petroleum companies for providing core materials. Thanks to T. Egler and the staff at Shell core warehouse for their generous help; to G. Herman, E. Stout, D. Stout, W. Dawson, R. Allen for core and petrophysical data; to L. S. Land for strontium and oxygen isotope analyses and beneficial discussions; to R. Koepnick for strontium isotope analyses; to R. Sassen, T. Dickson, J. S. Hanor, and J. L. Banner for discussion and comments; to J. T. Eldridge and F. C. Meendsen for discussions on depositional environments and core description; to R. D. Snelling for trace element analyses and beneficial discussions; to W. LeBlanc for x-ray diffraction analyses, S. Reed for providing technical assistance in the lab, K. Lyle for photography; to fellow graduate students S. O. Moshier, I. P. Gill, E. Tye, A. Roy, B. Nocita, P. Yuan, E. Chinn, M. DiMarco, P. Lowry, W. Ratliff, for making life go much easier during this research and for encouragements; to B. Delaville, M. Moore, F. Couvillon, C. Weber, S. Gum, L. Nichols, and L. Holt for keeping us all happy and for their logistical support; to all industrial associates members of the Applied Carbonate

Research Program for constructive comments at the annual meetings. Special thanks to Brian Carter, B. L. Kirkland, and W. J. Wade who read the dissertation and offered constructive comments. A very special thanks goes to M. L. Machain for her support and assistance during the course of this study. This research was supported by the Department of Geology, Applied Carbonate Research Program, and Basin Research Institute of the Louisiana State University.

To my mother, father, Kayvon, Mohammad, Maryam
and Maria

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
DEDICATION.....	iv
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
ABSTRACT.....	xvi

CHAPTER I

OVERVIEW AND SUMMARY OF THE DISSERTATION.....	1
GEOLOGIC SETTING.....	2
PREVIOUS STUDIES.....	4
PURPOSE OF THE RESEARCH.....	5
SUMMARY OF IMPORTANT CONCLUSIONS.....	6
REFERENCES CITED.....	11

CHAPTER II

BURIAL DIAGENESIS AND THERMOCHEMICAL SULFATE REDUCTION, SMACKOVER FORMATION, SOUTHEASTERN MISSISSIPPI SALT BASIN.....	16
ABSTRACT.....	17
INTRODUCTION.....	18
METHODS.....	21
PRE-HYDROCARBON MIGRATION BURIAL DIAGENESIS.....	23
POST-HYDROCARBON MIGRATION BURIAL DIAGENESIS.....	28
THERMOCHEMICAL SULFATE REDUCTION.....	33
CONCLUSIONS.....	38
ACKNOWLEDGEMENTS.....	39
REFERENCES CITED.....	40

CHAPTER III.

ASPECTS OF DIAGENESIS, GRAIN MINERALOGY, AND CALCITE CEMENT STRATIGRAPHY, UPPER SMACKOVER FORMATION, CLARKE COUNTY,

MISSISSIPPI.....	45
ABSTRACT.....	46
INTRODUCTION.....	48
ANALYTICAL METHODS.....	51
DEPOSITIONAL SETTING.....	55
LITHOFACIES OF THE UPPER SMACKOVER FORMATION.....	56
GRAIN TYPES OF THE UPPER SMACKOVER AND THEIR MINERALOGY.....	58
OOIDS.....	61
Algally Coated Grains.....	63
Cause of the Regional Gradients.....	65
EARLY DIAGENESIS.....	66
BURIAL DIAGENESIS.....	69
Calcite Cement.....	70
Sun #1G Board of Supervisors 16-13.....	72
Harmony Field.....	72
Pachuta Creek Field.....	77
East Nancy Field.....	91
Goodwater Field.....	97
Garland Creek Field.....	99
Saddle Dolomite and Late Anhydrite.....	99
Solid Bitumen.....	101
DEPTH OF CEMENTATION.....	105

OXYGEN AND CARBON ISOTOPIC COMPOSITIONS OF BURIAL CEMENTS.....	107
STRONTIUM ISOTOPIC COMPOSITIONS OF BURIAL CEMENTS.	77
TRACE ELEMENTS.....	110
BURIAL CEMENTATION HISTORY.....	117
CALCITE CEMENT STRATIGRAPHY.....	120
OXYGEN ISOTOPIC EVOLUTION OF SMACKOVER PORE WATER.	122
CONCLUSIONS.....	126
ACKNOWLEDGEMENTS.....	128
REFERENCES CITED.....	130

CHAPTER IV

DIAGENESIS GONE SOUR, AN EXAMPLE OF THE DIAGENETIC DESTRUCTION OF A JURASSIC HYDROCARBON RESERVOIR, BLACK CREEK FIELD, MISSISSIPPI SALT BASIN.....	145
ABSTRACT.....	146
INTRODUCTION.....	148
ANALYTICAL METHODS.....	150
GEOLOGIC SETTING OF BLACK CREEK FIELD.....	153
EARLY PRE-BURIAL DIAGENESIS AND POROSITY EVOLUTION.....	158
SHALLOW BURIAL DIAGENESIS AND POROSITY EVOLUTION..	166
Pre-Bitumen Calcite Cement.....	169
Saddle Dolomite and Late Anhydrite.....	174
Porosity Evolution During Shallow Burial Burial Diagenesis.....	182
DEEP BURIAL DIAGENESIS AND POROSITY EVOLUTION.....	185

Introduction.....	185
Calcitization of Late Anhydrite.....	186
Post-Bitumen Calcite Cement.....	191
Quartz Replacement.....	201
Fluorite.....	204
Pyrite.....	208
Elemental Sulfur.....	210
Porosity Evolution During Deep Burial Diagenesis.....	218
DISCUSSION.....	220
Oxygen Isotopes.....	220
Carbon Isotopes.....	225
Strontium Isotopes.....	228
Trace Elements.....	230
Cements.....	230
Ooids and Micrites.....	233
SIGNIFICANCE OF BLACK CREEK FIELD FOR HYDROCARBON PRESERVATION AND DESTRUCTION.....	235
CONCLUSIONS.....	238
ACKNOWLEDGEMENTS.....	240
REFERENCES CITED.....	242

CHAPTER V APPENDIX A

ANHYDRITE AND SULFUR DISTRIBUTION IN THE PHILLIPS

#1 JOSEPHINE.....	262
VITA.....	268

LIST OF TABLES

Table 2.1. Sulfur isotopic composition of anhydrite and elemental sulfur.....	37
Table 3.1. List of cores studied in Clarke County.....	53
Table 3.2. Trace elements and isotopic compositions of cements, Clarke County.....	75
Table 3.3. Trace elements and isotopic compositions of ooids, Clarke County.....	79
Table 3.4. Electron microprobe analyses of a zoned calcite cement, Clarke County.....	90
Table 4.1. Trace elements and isotopic compositions of dolomite, Black Creek field.....	163
Table 4.2. Point counting results of grainstone, Black Creek field.....	167
Table 4.3. Trace elements and isotopic compositions of shallow burial cements, Black Creek field.....	175
Table 4.4. Trace elements and isotopic compositions of allochems, Black Creek field.....	178
Table 4.5. Trace elements and isotopic compositions of deep burial cements, Black Creek field.....	192
Table 4.6. Oxygen isotopic composition of the late quartz, Black Creek field.....	205
Table 4.7. Point counting results of dolomite, Black Creek field.....	221

LIST OF FIGURES

Figure 1.1 Map of the major physiographic and tectonic features of the gulf rim.....	3
Figure 2.1. Location of the study area and thermal maturity of the Smackover Source facies.....	19
Figure 2.2. North-south geologic cross section across Mississippi salt basin.....	20
Figure 2.3. General paragenetic sequence for Smackover Formation.....	22
Figure 2.4 Pre-hydrocarbon migration calcite and saddle dolomite cements.....	24
Figure 2.5. Late replacement anhydrite.....	25
Figure 2.6. Solid bitumen cement.....	26
Figure 2.7. Carbon and oxygen isotopic compositions of allochems and diagenetic phases.....	27
Figure 2.8. Late anhydrite completely replaced by calcite.....	29
Figure 2.9. Late anhydrite partially replaced by calcite plus elemental sulfur.....	30
Figure 2.10. Post-bitumen calcite cement.....	31
Figure 3.1. Location map of Clarke County, Mississippi.....	49
Figure 3.2. Simplified stratigraphic column showing Upper Jurassic formations in Clarke County.....	50
Figure 3.3. Map of Clarke County showing the locations of the wells and fields.....	52

Figure 3.4. Depositional and diagenetic domains of the Smackover Formation, Clarke County.....	57
Figure 3.5. Isopach map of the upper Smackover Formation, Clarke County.....	59
Figure 3.6. Structure drawn on the top of the Smackover Formation, Clarke County.....	60
Figure 3.7. Paragenetic sequences for the upper Smackover Formation, Clarke County.....	67
Figure 3.8. Burial history curve of the top of the Smackover Formation, East Nancy field.....	71
Figure 3.9. Photomicrographs of zoned calcite cement, Sun #1G B. O. Supervisors.....	73
Figure 3.10. Photomicrographs of cement zones 3-4, Sun #1G Board of Supervisors.....	74
Figure 3.11. Photomicrographs of zoned calcite cement, Mosbacher #1 B. O. Supervisors 16-13.....	78
Figure 3.12. Photomicrographs of zoned calcite cement, Shell #1 Evans 26-6.....	81
Figure 3.13. Photomicrographs of post-compaction zoned calcite cement, Shell #1 Evans.....	84
Figure 3.14. Photomicrographs of post-compaction zoned calcite cement, Shell #1 Evans 26-6.....	85
Figure 3.15. Photomicrographs fracture filling calcite cement, Shell #1 Evans 26-6, 3,944 m.....	86
Figure 3.16. Photomicrograph of zoned calcite cement analyzed by microprobe, Shell #1 Evans.....	89

Figure 3.17. Photomicrographs of zoned calcite cement, E. Nancy field, Getty #1 Masonite 18-8....	92
Figure 3.18. Photomicrographs of post-compaction zoned calcite cement, Getty #1 Masonite 18-8.....	93
Figure 3.19. Photomicrographs of post-compaction calcite cement, Getty #1 Masonite 18-8.....	94
Figure 3.20. Photomicrographs of post-pressure solution calcite cement, Getty #1 Masonite 18-8...	95
Figure 3.21. Photomicrographs of fracture filling calcite cement, Getty #1 Reddoch 15-13.....	96
Figure 3.22. Photomicrographs of zoned calcite cement, Shell #1 Ruter.....	98
Figure 3.23. Photomicrographs of zoned calcite cement, Pruet & Hughes #1 Cooley 3-2.....	100
Figure 3.24. Photomicrographs of saddle dolomite Getty #1 Masonite 18-8.....	102
Figure 3.25. Photomicrographs calcite cement and saddle dolomite, Getty #1 Masonite 18-8.....	103
Figure 3.26. Photomicrographs of solid bitumen cement, Getty #1 Allen 20-7.....	104
Figure 3.27. Carbon and oxygen isotopic compositions of ooids and cements, Clarke County.....	108
Figure 3.28. Strontium isotopic compositions of calcite cements, East Nancy Field.....	109
Figure 3.29. Molar Mg/Ca ratios of pore waters as a function of depth in the Mississippi salt basin...	111

Figure 3.30. Average Mg contents of zones of a zoned calcite cement in Shell #1 Evans well.....	112
Figure 3.31. Average Mn contents of zones of a zoned calcite cement in Shell #1 Evans well.....	115
Figure 3.32. Patterns of zonation in calcite cements across Clarke County.....	118
Figure 3.33. Simplified diagenetic and hydrologic model, Clarke County.....	119
Figure 3.34. Postulated oxygen isotopic evolution of the Smackover pore waters, Clarke County.....	124
Figure 4.1. Location map of Black Creek Field.....	154
Figure 4.2. Stratigraphic column Phillips #1A Josephine and Phillips #1A Flurry wells.....	156
Figure 4.3. Burial history curve for the top of the Smackover Formation, Black Creek field.....	159
Figure 4.4. Paragenetic sequence of the Smackover Formation, Black Creek field.....	160
Figure 4.5. Photomicrograph of isopachous marine cement, Phillips #1A Josephine.....	162
Figure 4.6. Photomicrograph of chertified allochems, Phillips #1A Josephine.....	165
Figure 4.7. Photomicrographs of post-compaction pre-bitumen calcite cement, Phillips #1A Josephine....	170
Figure 4.8. Photomicrograph of pre-bitumen calcite cement, Phillips #1A Flurry.....	171
Figure 4.9. Photomicrograph of saddle dolomite and	

calcite cement Phillips #1A Josephine.....	172
Figure 4.10. Carbon-oxygen isotope plot of allochems and shallow burial cements, Black Creek field.....	176
Figure 4.11. Strontium isotope plot of allochems and shallow burial cements, Black Creek field.....	177
Figure 4.12. Photomicrograph of calcitized anhydrite and saddle dolomite, Phillips #1A Josephine.....	181
Figure 4.13. Vertical distribution of shallow burial cements, Phillips #1A Josephine.....	184
Figure 4.14. Photomicrograph of type one calcitized anhydrite, Phillips #1A Flurry.....	188
Figure 4.15. Photomicrograph of type two calcitized anhydrite, Phillips #1A Flurry.....	190
Figure 4.16. Carbon-oxygen plot of deep burial cements, Black Creek field.....	193
Figure 4.17. Photomicrographs of post-bitumen calcite cement in dolomite, Phillips #1A Flurry.....	194
Figure 4.18. Photomicrograph of post-bitumen calcite cement in grainstone, Phillips #1 Josephine.....	198
Figure 4.19. Strontium isotope compositions of deep burial cements, Black Creek field.....	200
Figure 4.20. Photomicrographs of late silica, Phillips #1A Josephine.....	202
Figure 4.21. Photomicrograph of Fluorite cement, Phillips #1A Flurry.....	207
Figure 4.22. SEM photograph of pyrite, Phillips	

#1A Josephine.....	209
Figure 4.23. Elemental sulfur phase diagram.....	211
Figure 4.24. Elemental sulfur viscosity variation with temperature.....	212
Figure 4.25. Photomicrographs of elemental sulfur, Phillips #1A Flurry.....	214
Figure 4.26. Porosity-permeability plot of grainstone and dolomite, Black Creek field.....	219
Figure 4.27. Postulated oxygen isotopic evolution of the Smackover pore water, Black Creek Field....	223
Figure 4.28. Simplified sketch showing sulfate- H_2S-S^0 -methane reaction cycle.....	237
Figure 5.1. Distribution of anhydrite in the Phillips #1A Josephine.....	164
Figure 5.2. Photomicrograph of calcitized anhydrite laths.....	165
Figure 5.3. Core photograph of massive replacement of the Smackover carbonate by anhydrite.....	166
Figure 5.4. Photomicrograph of anhydrite alteration to elemental sulfur.....	167

ABSTRACT

The Smackover Formation in the southeastern Mississippi salt basin has been buried to maximum depths of 3 to over 6 km and subjected to maximum temperatures of 100 to over 200 °C. This formation contains a lower laminated mudstone member, a middle mudstone to wackestone member, and an upper grainstone member.

In Clarke County, the upper Smackover member exhibits a north-south gradient in dolomite content, original mineralogy of ooids, and lithology. These regional gradients resulted from an increase in Mg/Ca concentrations of Smackover sea water northward across the carbonate platform.

Shallow burial diagenesis (<4.5 km) was dominated by calcite cementation. Calcite cements in Clarke County are luminescently zoned and exhibit a consistent sequence of luminescent zonation. However, the intensity of luminescence and number of zones in the calcite cements vary across the county. This is due to variation in the chemical composition of the host carbonate rock and local hydrology.

Deep burial diagenesis (>4.5 km and <7 km) is dominated by calcitization of anhydrite, precipitation of post-bitumen calcite cement, and formation of elemental sulfur. The chemical composition of post-bitumen calcite cement suggests precipitation from a pore water similar to the present Smackover brine.

The high temperature replacement of anhydrite by

calcite, the presence of post-bitumen calcite cement, the sulfur isotopic composition of sulfates and elemental sulfur, and the high concentration of hydrogen sulfide indicate that rapid thermochemical sulfate reduction of solid sulfate is taking place in the deep part of the Mississippi salt basin at temperatures of $>150^{\circ}\text{C}$.

Availability of large volumes of pore water during shallow burial and lack of a light carbon source resulted in progressive $\delta^{18}\text{O}$ depletion and constant $\delta^{13}\text{C}$ values in shallow burial calcite cements. Limited volumes of pore water during deep burial and incorporation of hydrocarbon-derived-light carbon generated by thermochemical sulfate reduction resulted in progressive $\delta^{18}\text{O}$ enrichment and $\delta^{13}\text{C}$ depletion in deep burial calcite cements.

Trace element composition of shallow and deep burial calcite cements indicates that the Sr/Ca and Mg/Ca ratios of associated pore waters increased and decreased, respectively, during burial.

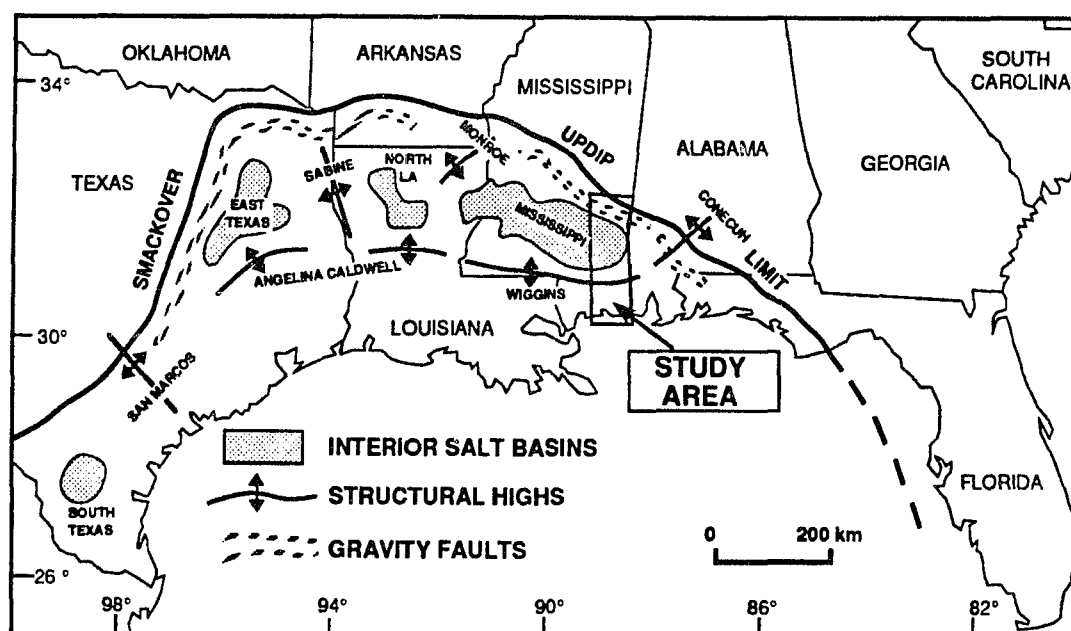
CHAPTER I

OVERVIEW AND SUMMARY OF THE DISSERTATION

GEOLOGIC SETTING

The Mississippi salt basin is one of four salt basins located around the northern rim of the Gulf of Mexico (Fig. 1). The salt basins formed in response to Early Mesozoic extension and continental break-up (Wood and Wapler, 1974; Buffler and Sawyer, 1985). The salt basins are separated from the Gulf of Mexico by a series of structural highs. Along their northern margins, they are bounded by a series of normal faults. The salt basins are separated from each other by fault bounded horst blocks (Fig. 1.1). Boundaries of the Mississippi salt basin are the Pickens-Gilbertown fault system to the north, Wiggins Arch to the south, the Monroe uplift to the west, and the Jackson graben to the east (Fig. 1.1). A maximum of 30,000 ft of sediments ranging in age from Early Jurassic to Holocene are present in the Mississippi salt basin (Williams, 1969). The lithologic sequence includes middle Jurassic evaporites of the Louann Salt and Werner Anhydrite and siliciclastics of the Norphlet Formation, Late Jurassic carbonates of the Smackover Formation and anhydrite and carbonates of the Haynesville Formation, and Late Jurassic, Cretaceous, and Tertiary siliciclastics with minor carbonates. Strata gently dip southward, as a result they are buried to greater depth in that direction. The Smackover Formation, for example, is buried to about 10,000 ft along the northern margin of the Mississippi salt basin, and to near 20,000 ft in the

Figure 1.1 Map showing the location of salt basins, major physiographic and tectonic features of the gulf rim, and the study area (Modified from Martin, 1978; Moore, 1984).



southern margin of the basin.

The Smackover Formation is a marine unit deposited in Late Jurassic time (Imley, 1980; Moore, 1984). This formation is informally divided into three members in this study. A lower laminated mudstone (30 ft thick), a middle laminated and burrowed mudstone-wackestone (300 ft thick), and an upper oolitic grainstone (300 ft thick).

PREVIOUS STUDIES

Oxley et al. (1967) and Dinkins (1968) gave general stratigraphic and lithologic descriptions of the Jurassic formations of the Mississippi salt basin. Badon (1973, 1974) conducted detailed lithofacies and environmental analysis of the Smackover Formation in Clarke County, Mississippi. Oglesby (1976) reported cathodoluminescence and trace element chemistry of calcite and dolomite cements of the upper Smackover member in Clarke and Smith counties. Wakelyn (1979) described detailed lithofacies characteristics of the Smackover Formation in Black Creek field near the southern margin of the basin. Moore (1984), Meendsen (1987), Meendsen et al. (1987), and Eldridge (1989) studied regional stratigraphy, lithofacies, and depositional environments of the Smackover Formation across the basin. Carpenter et al. (1974) and Kharaka et al. (1987) reported chemical compositions of pore waters in the Mississippi salt basin. Russell (1985) examined strontium isotopic compositions of

the pore waters in the basin. Sassen (1988), Sassen et al. (1987 a, b) and Sassen and Moore (1988) provided information on source rock characteristics, hydrocarbon migration, and hydrocarbon geochemistry in relation to burial history of the Smackover Formation in the Mississippi salt basin.

PURPOSE OF THE RESEARCH

Despite the cited investigations, a detailed regional synthesis of diagenesis and geochemistry of the Smackover Formation in the Mississippi salt basin has not been attempted. The present research was designed to define and examine the diagenetic characteristics of the Smackover Formation during progressive burial in the Mississippi salt basin (Chapter 2). This study is important because the Smackover Formation has been continuously buried in the Mississippi salt basin to depths of over 20,000 ft (6 km) and has been exposed to temperatures of over 200 °C. This depth and temperature range has seldom been considered in previous diagenetic studies and represents the transition between diagenesis and metamorphism.

Detailed consideration is given in Chapter 3 to the formation of zoned calcite cements in the shallow, northern part of the basin. Oglesby (1976) concluded that these zoned cements of the upper Smackover Formation formed shortly after burial, within a meteoric water lens. Studies of similar cements in the upper Smackover Formation in Arkansas

and Louisiana (Moore and Druckman, 1981; Moore, 1985) have suggested that these cements formed late from saline formation fluids. Determination of timing of cementation, environment of cementation, and variations in calcite cement luminescence across a carbonate platform was a major goal of the study.

A shortage of core materials from deeply buried Smackover carbonates (>15,000 ft) has resulted in a paucity of information about diagenetic processes which postdate hydrocarbon migration. Chapter 4 of the study presents a detailed examination of diagenesis of the Smackover Formation during deep burial and investigation of the effects of hydrocarbon migration and destruction on the diagenesis of this formation.

Finally, in Chapters 3 and 4 chemical characteristics of diagenetic phases were utilized to determine major changes in trace element content and stable and radiogenic isotopic signatures during progressive burial. These data were also used to postulate probable avenues of chemical evolution of pore waters in the Mississippi salt basin.

SUMMARY OF IMPORTANT CONCLUSIONS

Two separate diagenetic domains (one prior to, and one following hydrocarbon migration) with distinctly different processes and products have affected the Smackover Formation in the Mississippi salt basin. Pre-hydrocarbon migration

diagenesis was dominated by precipitation of calcite cement derived from pressure solution of host carbonate rock. The net result of this stage of diagenesis is destruction of porosity by cementation and by physical compaction. The post-hydrocarbon migration diagenetic phase was dominated by complex reactions involving thermochemical sulfate reduction and hydrocarbon oxidation. Diagenetic processes during post-hydrocarbon migration resulted in transformation of anhydrite to calcite and elemental sulfur. Elemental sulfur reacted with hydrocarbon gases producing non-hydrocarbon gases such as H_2S and CO_2 . Allowed to go to completion at depths of over 20,000 ft, these reactions were capable of totally destroying hydrocarbon reservoirs.

Replacement of anhydrite by calcite or calcite plus elemental sulfur occurred only at temperatures of 150 °C or greater. Because the upper limit of bacterially-influenced sulfate reduction is about 80 °C (Carothers and Kharaka, 1978; Trudinger et al., 1985), the reactions must be thermochemical. This conclusion is further supported by sulfur isotopic compositions of the sulfates and elemental sulfur. Elemental sulfur shows no evidence of fractionation by biologically-mediated processes as occurs in shallow sulfur deposits (Davis and Kirkland, 1979). Occurrence of thermochemical sulfate reduction at temperatures of <200 °C has been questioned (Trudinger et al., 1985). This finding cleared doubts relative to the occurrence of this process at

temperatures of <200 °C.

The Smackover Formation exhibits distinct gradients with respect to ooid mineralogy, dolomite content, lithology, and intensity of early and late diagenetic processes across the Smackover carbonate platform. The inferred presence of originally aragonitic ooids on the northern part of the platform, originally calcitic ooids on the southern part of the platform, and mixed calcite-aragonite ooids in the central part of the platform is best explained by a north-to-south gradient in Mg/Ca ratio and salinity of Smackover sea water. Previously reported secular variations in mineralogy of abiotic carbonates suggest that Jurassic ooids should be calcitic, perhaps as a result of high partial pressure of CO₂ in the Jurassic atmosphere and oceans (Sandberg, 1983). The mineralogical gradient of Smackover ooids across the platform indicates that changes in Mg/Ca ratio, salinity, and secular variations in partial pressure of CO₂ were all both important in controlling the mineralogy of abiotic carbonate minerals in the geologic record.

Meyers (1974, 1978), studying zoned calcite cements in Paleozoic carbonate rocks of New Mexico, correlated cement luminescent zones across distances up to 150 km. The major conclusions of Meyers' study is that his zones formed simultaneously within a continuous aquifer under invariant chemical conditions. Luminescently zoned calcite cements in

the northern part of the present study area formed after the initiation of pressure solution. The sequence of zonation was similar in all calcite cements across the study area. However, the number of zones and the intensity of zonation varies significantly across the platform. This suggests that zoned calcite cements of the Smackover Formation were influenced by local diagenetic conditions. It is inferred that variations in luminescent zonation were influenced by the composition of the host carbonates and by the local hydrologic regime. This interpretation provides an alternative explanation for luminescently zoned calcite cements which can not be correlated for long distances.

Smackover calcite cements exhibit an initial depletion trend followed by an enrichment trend in $\delta^{18}\text{O}$ composition. The preferred interpretation of the observed trend is: (1) during shallow burial when sufficient pore water is available, temperature dependent calcite-water fractionation decreases $\delta^{18}\text{O}$ in calcite and increases that in pore water; (2) during progressive burial, reduction of porosity decreases water/rock ratio, causing the diagenetic system to ultimately become rock dominated. During this stage of diagenesis pore waters with high $\delta^{18}\text{O}$ compositions, combined with the effects of rock buffering seem to negate calcite-water temperature fractionation effects, leading to the observed high $\delta^{18}\text{O}$ values in deep burial calcite cements.

Carbon isotopic composition of calcite cements precipitated during shallow burial is similar to that of primary grains and does not vary. This may be the result of buffering of carbon isotopic compositions of pore water by the host carbonates. In contrast, calcite cements precipitated during deep burial exhibit low $\delta^{13}\text{C}$ because of incorporation of light carbon derived from thermochemical destruction of hydrocarbons.

Strontium isotopic compositions of calcite and dolomite cements in the shallower part of the basin become more radiogenic in younger cements, suggesting introduction siliciclastic-influenced waters to the Smackover Formation. In contrast, strontium isotopic compositions of cements in the deeper part of the basins are consistently close to that of Late Jurassic sea water. This indicates closed system diagenesis in the deep part of the basin, without introduction of waters containing radiogenic strontium isotope.

REFERENCES CITED

- Badon, C. L., 1973, Petrology of the Norphlet and Smackover Formations (Jurassic), Clarke County, Mississippi: Unpublished dissertation, Louisiana State University, 197 p.
- 1974, Petrology and reservoir potential of the upper member of the Smackover Formation, Clarke County, Mississippi: Gulf Coast Association of Geological Societies Transactions, v. 24, p. 163-174.
- Buffler, R. T., and Sawyer, D. S., 1985, Distribution of crust and early history, Gulf of Mexico basin: Gulf Coast Association of Geological Societies, v. 35, p. 333-344.
- Carpenter, A. B., Trout, M. L., and Pickett, E. E., 1974, Preliminary report on the origin and chemical evolution of lead and zinc brines in central Mississippi: Economic Geology, v. 69, p. 1191-1206.
- Carothers, W. W., and Kharaka, Y. K., 1978, Aliphatic acids anions in oil-field waters- implications for origin of natural gas: AAPG Bulletin, v. 62, p. 2441-2453.
- Choquette, P. W., and James, N. P., 1987, Diagenesis #12. Diagenesis in limestones-3. The deep burial environment: Geoscience Canada, v. 14, p. 3-35.
- Davis, J. B., and Kirkland, D. W., 1970, Biogenic sulfur depositions: Economic Geology, v. 74, p. 462-468.
- Dinkins, T. H., 1968, Jurassic stratigraphy of central and

- southern Mississippi: Mississippi Geological Survey Bulletin, v. 109, p. 9-37.
- Eldridge, J. T., Upper Jurassic stratigraphy, porosity distribution, and hydrocarbon potential of western southern Mississippi: Unpublished M.S. thesis Louisiana State University, 179 pp.
- Imlay, R. W., 1980, Jurassic paleobiography of the conterminous United States in its continental setting: USGS Professional Paper 1062, 134 pp.
- Kharaka, Y. K., Maest, A. S., Carothers, W. W., Law, L. M., Lamouthe, P. J., and Fries, T. L., 1987, Geochemistry of metal-rich brines from central Mississippi salt dome basin, U.S.A.: Applied Geochemistry, v. 2, p. 543-508.
- Martin, R. G., 1978, Northern and eastern Gulf of Mexico continental margin: stratigraphy and structural framework, in Bouma, A. H., Coleman, J. M., eds., Framework, Facies, and oil-trapping characteristics of the upper continental margin: AAPG Studies in Geology #7, p. 21-42.
- Meendsen, F. C., 1987, Upper Jurassic stratigraphy, porosity distribution, and hydrocarbon potential of eastern southeast Mississippi: M.S. thesis, Louisiana State University, 187 pp.
- Moore, C. H., Heydari, E., and Sassen, R., 1987, Upper Jurassic depositional system and hydrocarbon potential of southern Mississippi: Gulf

Coast Association of Geological Societies Transactions,
v. 37, p. 161-174.

Meyers, W. J., 1974, Carbonate cement stratigraphy of the
Lake Valley Formation (Mississippian) Sacramento
Mountains, New Mexico: Journal of Sedimentary
Petrology, v. 44, p. 837-861.

----- 1978, Carbonate cements: their regional
distribution and interpretation in Mississippian
limestones of southwestern New Mexico: Sedimentology,
v. 25, p. 371-400.

Moore, C. H., 1984, The upper Smackover of the Gulf rim:
Depositional system, diagenesis, porosity evolution and
hydrocarbon production, in Ventress, W. P. S., Bebout,
D. G., Perkins, R. F., and Moore, C. H., eds., The
Jurassic of the Gulf Rim: Proceedings of third annual
research conference of SEPM, Baton Rouge, Louisiana, p.
283-308.

----- 1985, Upper Jurassic subsurface cement- a case
history, in Schneiderman, N., and Harris, P. M., eds.,
Carbonate cements: SEPM Special Publication 36, p. 291-
308.

----- and Druckman, Y., 1981, Burial diagenesis and
porosity evolution, Upper Jurassic Smackover, Arkansas
and Louisiana: American Association of Petroleum
Geologists Bulletin, v. 65, p. 597-628.

----- Chowdhury, A., and Heydari, E., 1986, Variation

- of ooid mineralogy in Jurassic Smackover limestone as control of ultimate diagenetic potential: American Association of Petroleum Bulletin: v. 70, p. 622-628.
- Oglesby, T. W., 1976, A model for the distribution of manganese, iron, and magnesium in authigenic calcite and dolomite cements in the Upper Smackover calcite in eastern Mississippi: Unpublished M.Sc. thesis, University of Missouri, Columbia, MO, 122 pp.
- Oxley, M. L., Minihan, E., and Ridgeway, J. M., 1967, A study of the Jurassic sediments in portions of Mississippi and Alabama: Gulf Coast Association of Geological Societies Transactions, v. 17, p. 24-48.
- Russell, C. W., 1985, a strontium isotope study of oil field brines and associated rocks in southeastern Mississippi: Unpublished M.S. thesis, Florida State University, 176 pp.
- Sandberg, P. A., 1983, An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy: Nature, v. 305, p. 19-22.
- Sassen, R. 1988, Geochemistry and carbon isotopic studies of crude oil destruction, bitumen precipitation, and sulfate reduction in the deep Smackover Formation: Organic Geochemistry, v. 12, p. 351-361.
- Moore, C. H., Meendsen, F. C., 1987 a, Distribution of hydrocarbon source potential in the Jurassic Smackover Formation: Organic Geochemistry, v.

11, p. 379-383.

----- Moore, C. H., Nunn, J. A., Meendsen, F. C., and Heydari, E., 1987 b, Geochemical studies of crude oil generation, migration, and destruction in the Mississippi salt basin: Gulf Coast Association of Geological Societies, v. 37, p. 217-224.

----- and Moore, C. H., 1988, Framework of hydrocarbon generation and destruction in eastern Smackover trend: American Association of Petroleum Geologists Bulletin, v. 72, p. 649-663.

Trudinger, P. A., Chambers, L. A., and Smith, J. W., 1985, Low-temperature sulfate reduction: Biological versus abiological: Canadian Journal of Earth Sciences, v. 22, p. 1910-1918.

Wakelyn, B. D., 1977, Petrology of the Smackover Formation (Jurassic): Perry and Stone counties, Mississippi: Gulf Coast Associations of Geological Societies Transactions, v. 27, p. 379-417.

Williams, C. H., Jr., 1969, Cross section from Mississippi-Tennessee state line to Horns Island in Gulf of Mexico: Jackson, Mississippi, Mississippi Geological Survey.

Wood, M., and Wapler, A., 1974, The evolution of the interior Mesozoic basin and the Gulf of Mexico: Gulf Coast Association of Geological Societies Transactions, v. 24, p. 31-41.

CHAPTER II

BURIAL DIAGENESIS AND THERMOCHEMICAL SULFATE REDUCTION, SMACKOVER FORMATION, SOUTHEASTERN MISSISSIPPI SALT BASIN

(Reprint of a paper by Ezat Heydari and Clyde H. Moore,
1989: Geology, v. 17, p. 1080-1084. With the premission of
the Geological Society of America)

ABSTRACT

The Smackover Formation in the southeastern Mississippi salt basin has been buried from 3 to 6 km and subjected to temperatures of 100 to 200 °C. This formation exhibits two distinct phases of burial diagenesis, one pre-hydrocarbon migration, and the other post-hydrocarbon migration.

Pre-hydrocarbon migration burial diagenesis is characterized by precipitation of calcite cement followed by saddle dolomite and late anhydrite. These phases formed at temperatures of less than 100 °C. The oxygen isotopic composition of calcite ranges from -5‰ to -8.4‰ PDB, and carbon isotopic composition ranges from $+3.5\text{‰}$ to $+6.0\text{‰}$ PDB. The sulfur isotopic composition of late anhydrites ranges from $+18.1\text{‰}$ to $+19.1\text{‰}$ CDT.

Post-hydrocarbon migration burial diagenesis is dominated by replacement of previously formed late anhydrite by calcite or calcite plus elemental sulfur, and precipitation of post-bitumen calcite cement. These diagenetic phases formed at temperatures above 150 °C and are present only in the deep part of the basin. The oxygen isotopic compositions of calcites that replace anhydrite range from -3.0‰ to -4.0‰ PDB, and carbon isotopic compositions range from -2.0‰ to $+4.2\text{‰}$ PDB. The oxygen isotopic compositions of post-bitumen calcites range from -3.4‰ to -5.6‰ PDB and carbon isotopic compositions range from -1.6‰ to -16.3‰ PDB. Two samples of elemental

sulfur have sulfur isotopic compositions of $+15.8\text{‰}$ and $+16.1\text{‰}$ CDT.

The light carbon isotopic compositions of post-bitumen calcite cement indicate that carbon incorporated in this cement was partly derived from thermal oxidation of hydrocarbon gases. The relatively heavy oxygen isotopic compositions of these cements suggest precipitation from pore waters with a heavy oxygen isotopic composition.

The high-temperature replacement of anhydrite by calcite, the presence of post-bitumen calcite cement, the sulfur isotopic composition of sulfates and elemental sulfur, and the high concentration of hydrogen sulfide indicate that thermochemical reduction of solid sulfates is taking place in the deep part of the Mississippi salt basin at temperatures as low as $150\text{ }^{\circ}\text{C}$.

INTRODUCTION

The Smackover Formation in the southeast Mississippi salt basin is a marine unit of Late Jurassic age (Figs. 2.1 and 2.2). The formation is composed of a lower laminated limestone member deposited in a deep, anoxic, and hypersaline environment, and an upper oolitic grainstone member that represents deposition in a shallow, high-energy, mobile shoal complex (Meendsen et al., 1987). The Smackover hydrocarbon source facies (lower laminated member) is thermally immature in the northernmost part of the basin, is

Figure 2.1. Study area includes Clarke, Wayne, Greene, Perry, George, Stone, Jackson, and Harrison counties. Thermal maturity data are from Sassen and Moore (1988). BCF: Black Creek field; ENF: East Nancy field; GWF: Goodwater field; WF: Winchester field.

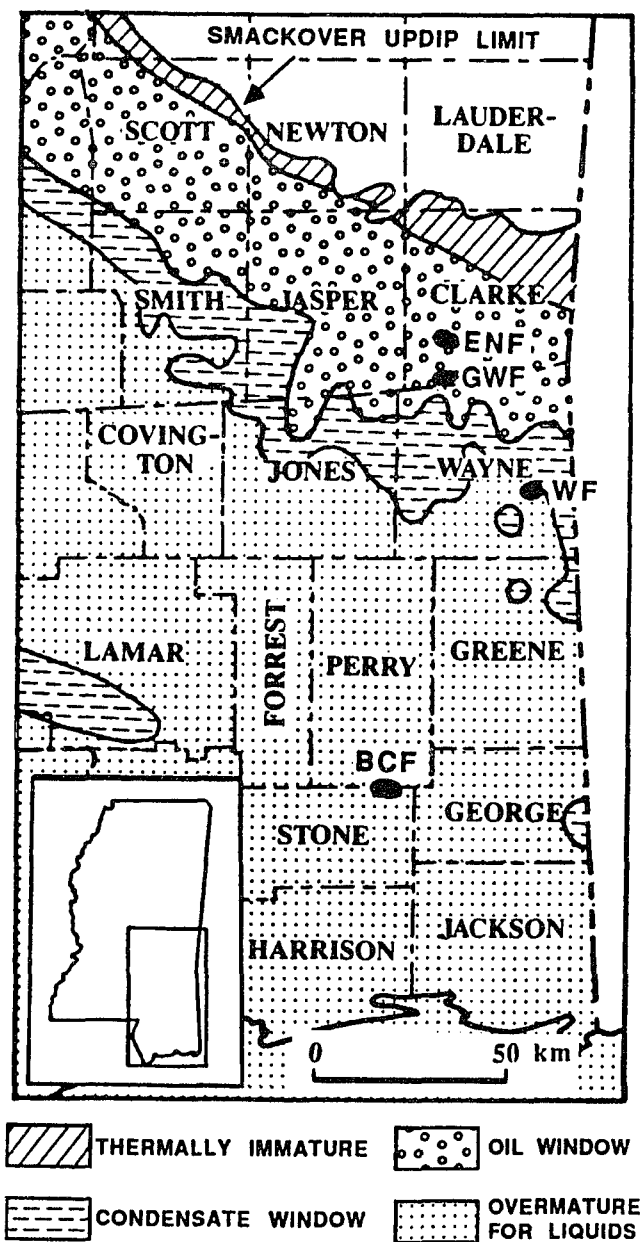
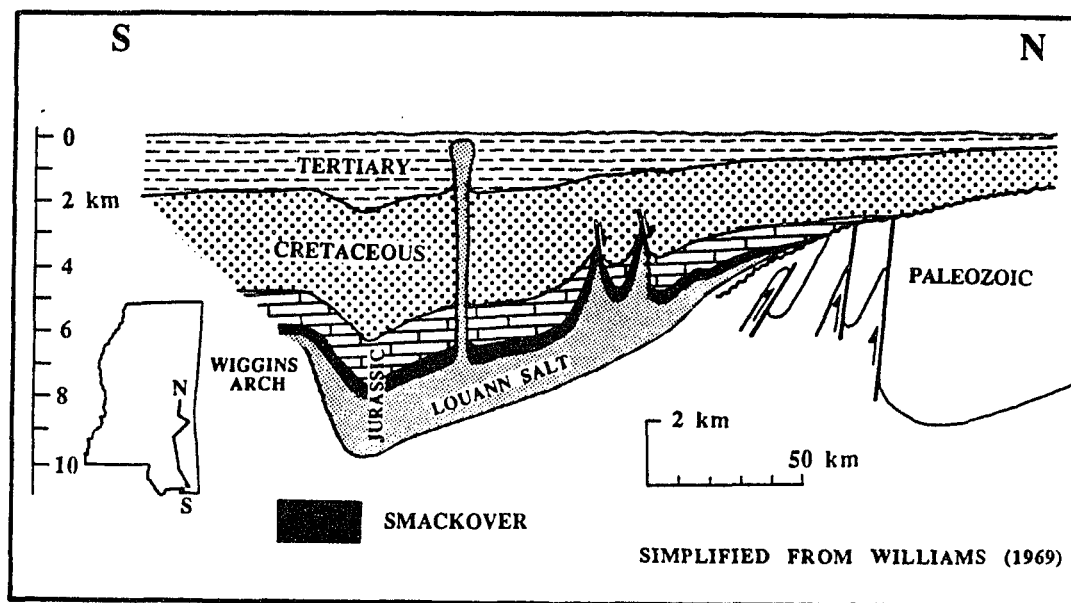


Figure 2.2. North-south geologic cross section across Mississippi salt basin (simplified from Williams, 1969).



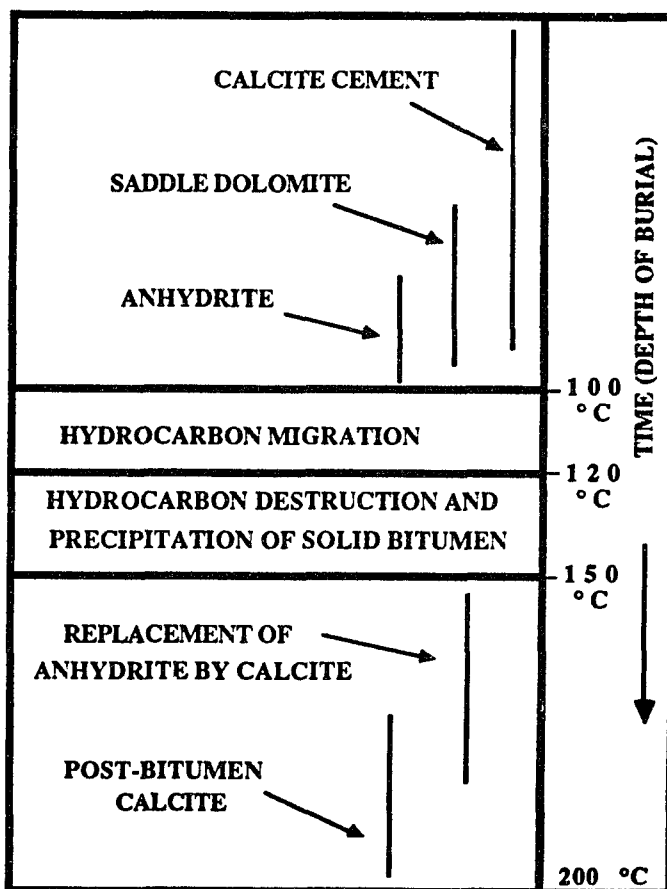
within the liquid hydrocarbon window to the south, and is overmature for liquid hydrocarbons in the deep part of the basin (Sassen et al., 1987; Sassen and Moore, 1988) (Fig. 2.1).

The Smackover Formation has been buried from 3 km in the north to over 6 km in the southern part of the basin (Fig. 2.2), and has been subjected to temperatures ranging from 100 °C to over 200 °C. In the study area, this formation exhibits two distinct phases of burial diagenesis: one pre-hydrocarbon migration, and the other post-hydrocarbon migration (Fig. 2.3). The chemical characteristics and occurrences of these deep burial diagenetic phases provide information on the temperature, timing, and mechanism of thermochemical sulfate reduction and hydrocarbon destruction in the Smackover Formation in the Mississippi salt basin.

METHODS

The observations presented here were made on polished and stained petrographic thin sections. Samples for isotopic analyses were collected either under a binocular microscope or drilled out by a Jensen milling machine. All samples were X-rayed from 20° to 32° 2 θ with CuK α radiation to detect 100% reflection peaks of calcite, dolomite, anhydrite, celestite, and strontianite. Isotopic analyses were performed on pure samples by Coastal Science Laboratories,

Figure 2.3. General paragenetic sequence for Smackover Formation in study area with approximate temperature ranges of events shown.



Austin, Texas, using standard techniques. Precision of the analyses is $\pm 0.2\text{‰}$ for carbon and oxygen and $\pm 0.3\text{‰}$ for sulfur isotopes.

PRE-HYDROCARBON MIGRATION BURIAL DIAGENESIS

This stage of burial diagenesis of the Smackover Formation is characterized by precipitation of calcite cement followed by saddle dolomite and late anhydrite (Figs. 2.3, 2.4, 2.5). This is similar to diagenesis observed in the Smackover Formation in Arkansas and Louisiana by Moore and Druckman (1981) and Moore (1985). Nearly all pre-hydrocarbon migration calcite cements postdate pressure solution (Fig. 2.4), and therefore precipitated during burial at elevated temperatures. Arrival of liquid hydrocarbons and precipitation of solid bitumen (Fig. 2.6) temporarily retarded further precipitation of calcite, dolomite, and anhydrite cements in the Smackover Formation.

The oxygen isotopic compositions of pre-hydrocarbon migration calcite cements range from -5‰ to -8.4‰ relative to Peedee belemnite (PDB) standard (Fig. 2.7). The carbon isotopic compositions of the calcite cements range from $+3.5\text{‰}$ to $+6.0\text{‰}$ PDB, which is similar to the carbon isotopic composition of the Smackover allochems (ooids and algal coated grains) (Fig. 2.7).

The trend in the oxygen isotopic compositions of the pre-hydrocarbon migration calcite cements toward depleted

Figure 2.4. Pre-hydrocarbon migration calcite (C) and saddle dolomite (SD) cements. Note that both postdate pressure solution at grain contacts (Phillips #1A Josephine, 5863.0 m, Black Creek field).

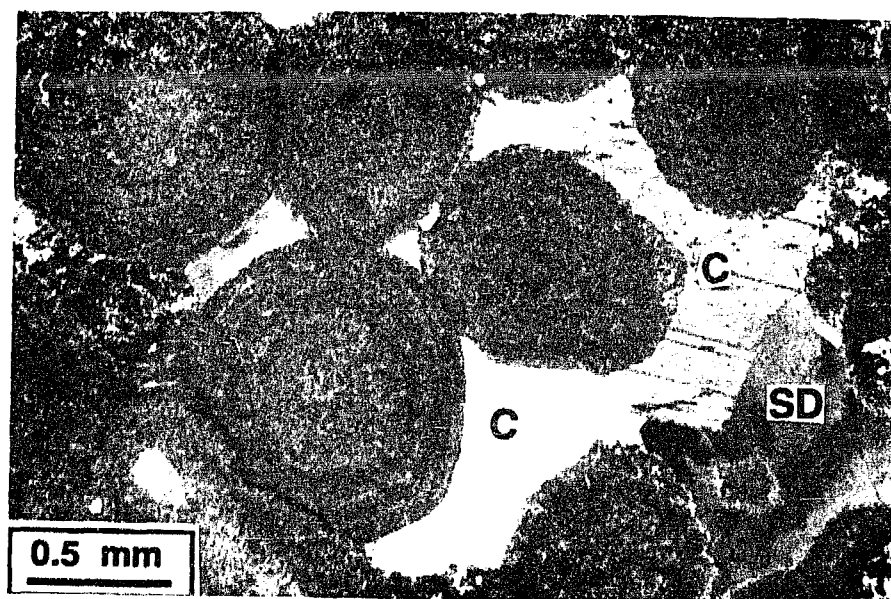


Figure 2.5. Late replacement anhydrite (Shell #1 Ruter, 4734.2 m, Goodwater field). Anhydrite (A) is unaltered at reservoir temperature of 120 °C.

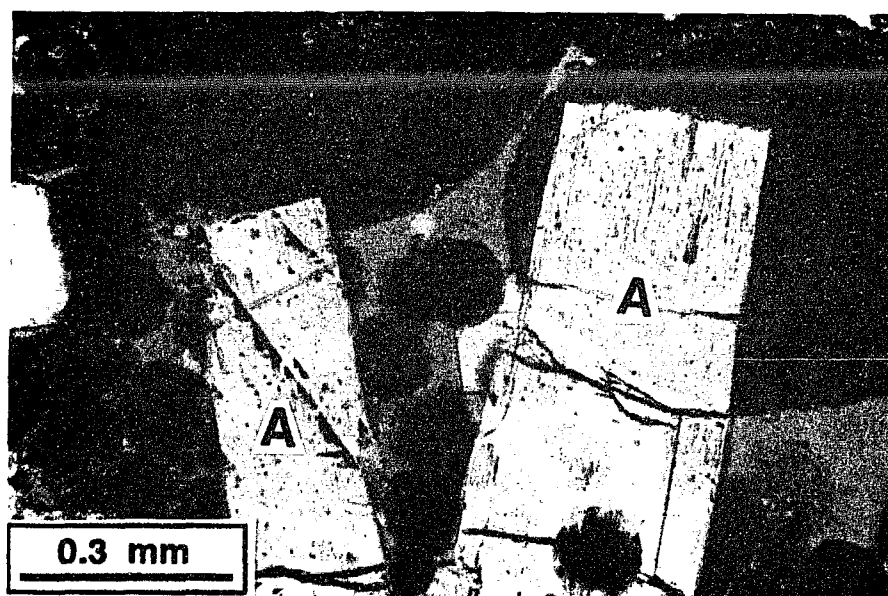


Figure 2.6. Emplacement of hydrocarbons and precipitation of solid bitumen (B) ended precipitation of pre-hydrocarbon migration calcite cement (C) (Getty #1 Allen 20-7, 4131.8 m, East Nancy field). P: pore space.

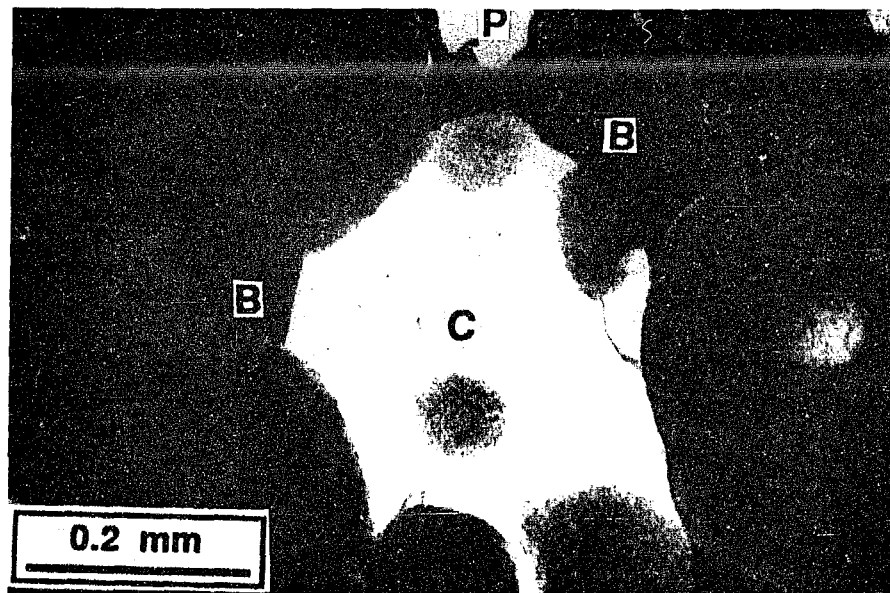
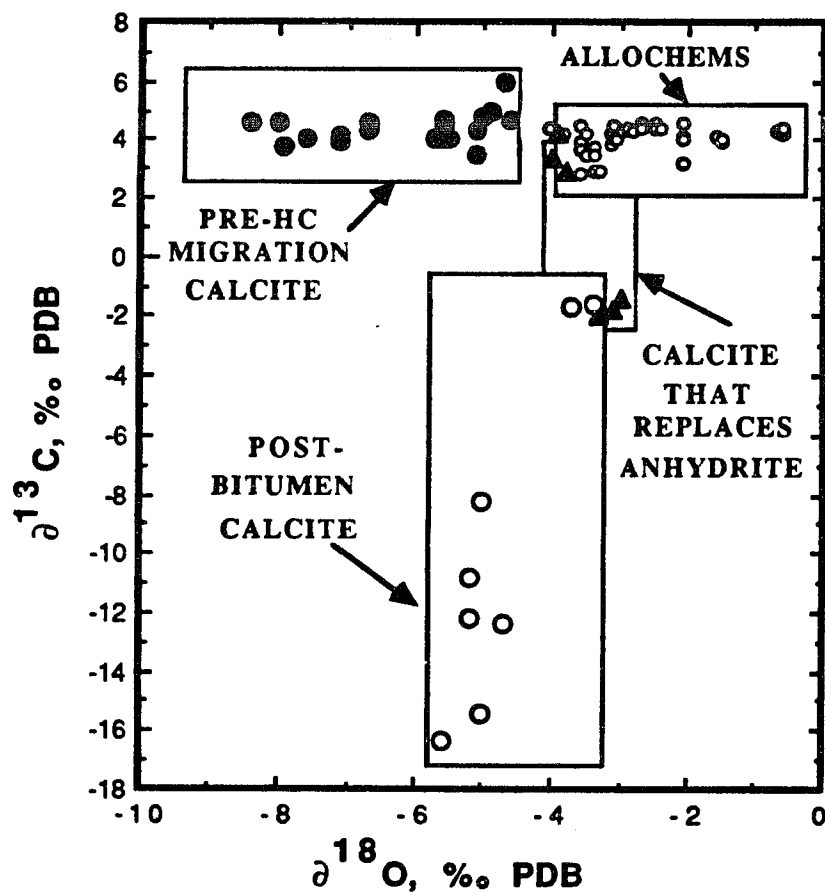


Figure 2.7. Carbon and oxygen isotopic compositions of allochems and diagenetic phases of the Smackover Formation in study area. HC: hydrocarbon.



values (Fig. 2.7) indicates precipitation at progressively higher temperatures during burial. The similarity of the carbon isotopic compositions of these calcites to that of the Smackover allochems (Fig. 2.7) indicates that the carbon of the calcite was derived and buffered by the host carbonate rock.

POST-HYDROCARBON MIGRATION BURIAL DIAGENESIS

The most important post-hydrocarbon migration burial diagenetic events (Fig. 2.3) are replacement of previously formed late anhydrite by calcite (Fig. 2.8) or by calcite plus elemental sulfur (Fig. 2.9), and precipitation of a post-bitumen calcite cement (Fig. 2.10).

Replacement of anhydrite by calcite, or by calcite plus elemental sulfur, only occurs in wells with formation temperatures greater than 150 °C. We therefore conclude that this process must have been initiated at temperatures of at least 150 °C.

Post-bitumen calcite cements contain inclusions of pyrobitumen and postdate cracks formed in the pyrobitumen (Fig. 2.10). The main phase of soluble solid bitumen precipitation (Fig. 2.6) is seen in wells with formation temperatures greater than 120 °C. Complete transformation of soluble solid bitumen to insoluble pyrobitumen is seen in wells with formation temperatures greater than 170 °C. Post-bitumen calcite cements postdate pyrobitumen formation (Fig.

Figure 2.8. Late anhydrite completely replaced by calcite (AC) (Phillips #1A Josephine, 5869.7 m, Black Creek field). Compare with unaltered anhydrite in Figure 2.5.

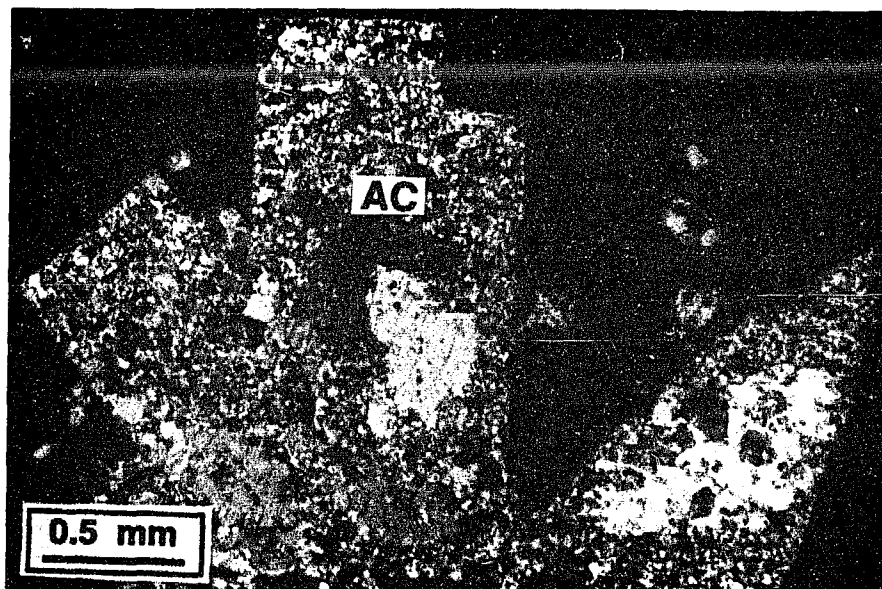


Figure 2.9. Late anhydrite (A) partially replaced by calcite (C) plus elemental sulfur (S) (Phillips #1A Flurry, 6059.1, Black Creek field). Note anhydrite inclusions in calcite and elemental sulfur inclusions in anhydrite.

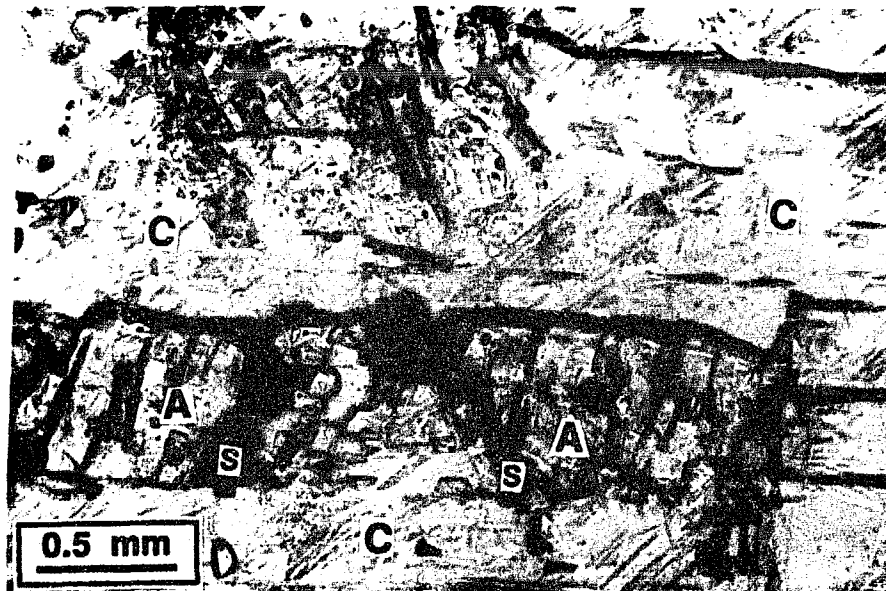
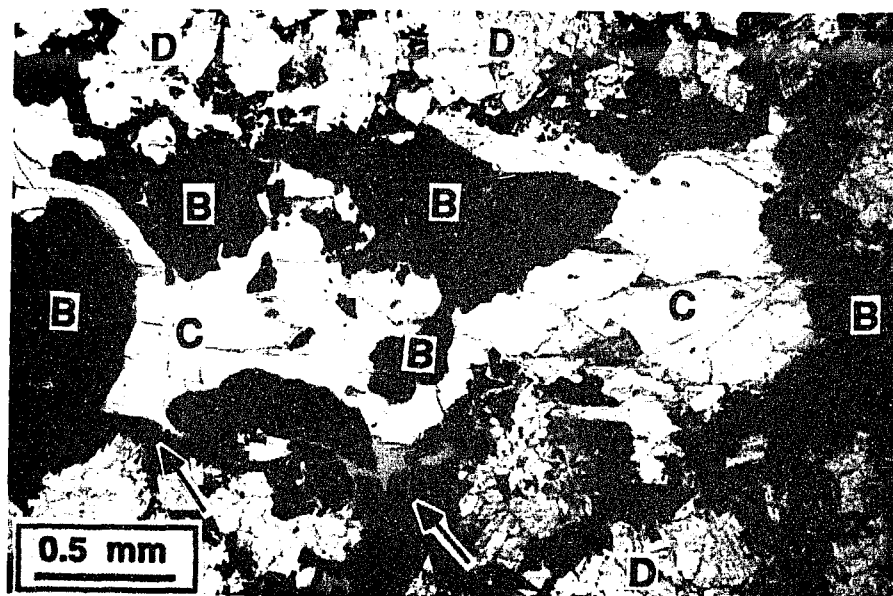


Figure 2.10. Post-bitumen calcite cement (C) (Phillips #1A Flurry, 6028.5 m, Black Creek field). Note inclusions of pyrobitumen (B) in calcite. Calcite cement heals cracks (arrow) formed in pyrobitumen. D: dolomite.



2.10), and therefore precipitated very late at temperatures of 150 °C or greater.

The carbon isotopic compositions of calcite that replaces anhydrite range from -2.0‰ to $+4.2\text{‰}$ PDB, and oxygen isotopic compositions range from -3.0‰ to -4.0‰ PDB (Fig. 2.7). The carbon isotopic compositions of the post-bitumen calcite cements range from -1.6‰ to -16.3‰ PDB, and oxygen isotopic compositions range from -3.4‰ to -5.6‰ PDB (Fig. 2.7).

The carbon isotopic compositions of post-bitumen calcite cements are significantly lighter than the pre-hydrocarbon migration calcite cements (Fig. 2.7). The time and temperature of formation of the post-bitumen calcite cements are compatible with the derivation of isotopically light carbon from hydrocarbon gases that were produced by thermal degradation of liquid hydrocarbons. Most previously reported calcites with isotopically light carbon are related to bacterial degradation of organic compounds at low temperatures and shallow depths (Hovland et al., 1987; Ritger et al., 1987).

The oxygen isotopic composition of the post-bitumen calcite cements (-3.4‰ to -5.6‰ PDB) and calcite that replaces anhydrite (-3.0‰ to -4.0‰ PDB) are heavier than pre-hydrocarbon migration calcite cements (-5‰ to -8.4‰ PDB), despite the fact that post-bitumen calcite cement and calcite that replaces anhydrite precipitated at

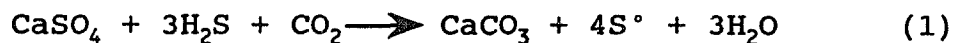
significantly higher temperatures. This may indicate that during pre-hydrocarbon migration burial diagenesis in shallow burial, high porosity and relatively high water/rock ratio resulted in progressive $\delta^{18}\text{O}$ depletion in precipitating cements and simultaneous $\delta^{18}\text{O}$ enrichment in the pore waters due to carbonate-water temperature dependent oxygen isotope fractionation. Later, during post-hydrocarbon migration burial diagenesis, porosity and water/rock ratio decreased significantly, although pore water $\delta^{18}\text{O}$ enrichment continued. Therefore, the relatively heavy $\delta^{18}\text{O}$ composition of post-hydrocarbon migration cements reflects buffering by the host carbonate rocks in a low water/rock system as well as precipitation from pore waters with high $\delta^{18}\text{O}$ composition (Heydari and Moore, 1988).

THERMOCHEMICAL SULFATE REDUCTION

Sulfate reduction can occur either at low temperatures (<100 °C) by the biochemical action of bacteria, or at high temperatures as a result of thermochemical processes (Trudinger et al., 1985; Machel, 1988). Although bacterial sulfate reduction is well documented, the temperature and nature of thermochemical sulfate reduction are relatively uncertain (Trudinger et al., 1985). Hydrogen sulfide concentration in hydrocarbon gases generally increases with increasing temperature in carbonate- and sulfate-dominated reservoirs (Anisimov, 1978; Orr, 1977). The gases of the

Smackover reservoir at Black Creek field (Fig. 2.1), for example, are composed of 78% H_2S at a depth of 6 km and a formation temperature of 205 °C (Parker, 1974). Generation of large volumes of hydrogen sulfide in hydrocarbon reservoirs is likely only through conversion of reservoir sulfate to sulfide (Orr, 1974, 1977). Experimental studies of the thermochemical reduction of solid sulfates have not been successful at temperatures less than 200 °C (Trudinger et al., 1985). However, on the basis of geologic observations and thermodynamic calculations, temperatures ranging from 80 to 150 °C have been suggested for the initiation of thermochemical sulfate reduction (Orr, 1974, 1977; Anisimov, 1978; Siebert, 1985; Krouse et al., 1988; Sassen, 1988).

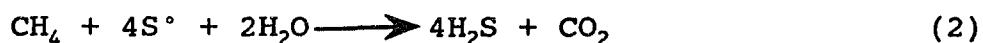
Two lines of evidence can be used to document the occurrence of thermochemical sulfate reduction in the Smackover Formation in the Mississippi salt basin. The first is high temperature replacement of solid sulfate by calcite (Figs. 2.8 and 2.9), which results from thermochemical breakdown of solid sulfate, and can be shown by reaction 1 (Siebert, 1985):



The coexistence of anhydrite + calcite + elemental sulfur (Fig. 2.9) indicates that this reaction was not complete when the wells were drilled or, alternatively, the system was at thermodynamic equilibrium under the existing

fugacities of H_2S , CO_2 , and H_2O . The carbon isotopic composition of the calcite that replaces anhydrite (-1.7‰ to $+4.2\text{‰}$ PDB) indicates that reduction of sulfate to elemental sulfur occurred by reaction with hydrogen sulfide (Orr, 1974, 1977) and not by oxidation of hydrocarbon gases. Furthermore, the CO_2 for the formation of this calcite was mostly derived from decomposition of carbonate host rock. Anhydrite replacement by calcite has also been well documented for bacterial sulfate reduction (Davis and Kirkland, 1970, 1979; Kirkland and Evans, 1976; Pierre and Rouch, 1988). These authors reported carbon isotopic compositions ranging from -5‰ to -40‰ PDB for calcite produced by low temperature bacterial reduction of sulfates. These values are significantly lighter than those for calcite that replaces anhydrite reported in this study.

Post-bitumen calcite is precipitated as a passive pore-filling cement (Fig. 2.10) rather than as replacement of other phases. This calcite could have been influenced by oxidation of methane or other hydrocarbon gases by elemental sulfur (reaction 2).



The carbon isotopic composition of the post-bitumen calcite cement (-1.6‰ to -16.3‰ PDB) is depleted relative to other cements and is consistent with minor contribution from methane oxidation.

The second line of evidence for thermochemical sulfate

reduction is the sulfur isotopic composition of depositional anhydrite, late diagenetic anhydrite, and elemental sulfur. Jurassic depositional sulfate (Buckner Anhydrite) has sulfur isotopic compositions ranging from $+15.6\text{‰}$ to $+17.1\text{‰}$ (average = $+16.4\text{‰}$) relative to the Canyon Diablo troilite (CDT) standard (Table 2.1). This is close to the sulfur isotopic composition of Late Jurassic sea water (Claypool et al., 1980). Late diagenetic anhydrites of the Smackover Formation have isotopic composition of $+18.1\text{‰}$ to $+19.0\text{‰}$ CDT with an average of $+18.6\text{‰}$ (Table 2.1). Two samples of elemental sulfur have sulfur isotopic compositions of $+15.8\text{‰}$ and $+16.1\text{‰}$ CDT (Table 2.1). These data suggest that sulfate contained in the late diagenetic anhydrite was recycled from Jurassic depositional anhydrite. In addition, the similar sulfur isotopic compositions of elemental sulfur and reservoir sulfates (diagenetic and depositional) and the presence of elemental sulfur inclusions in anhydrite (Fig. 2.9) strongly suggest a thermochemical origin for the elemental sulfur.

Experimental studies indicate that thermochemical reduction of solid sulfate requires a high concentration of sulfate ions and low pH (Trudinger et al., 1985). In addition, the rate of reaction is very slow at temperatures below $200\text{ }^{\circ}\text{C}$. Sulfate concentrations in subsurface waters of the Mississippi salt basin and other basins are generally very low, and the pH of these waters ranges from 5 to 6

TABLE 2.1. SULFUR ISOTOPIC COMPOSITIONS OF EARLY AND LATE
ANHYDRITES AND ELEMENTAL SULFUR

Location	Depth (m)	$\delta^{34}\text{S} (‰) \text{ CDT}$
Early depositional anhydrite		
Black Creek field	5823.3	+17.1
Black Creek field	5821.8	+16.7
Winchester field	4621.8	+15.6
Winchester field	4623.0	+16.1
Late diagenetic anhydrite		
Black Creek field	5982.1	+18.1
Black Creek field	5977.3	+19.1
Winchester field	4324.2	+18.4
Winchester field	4370.1	+19.0
Elemental sulfur		
Black Creek field	6059.1	+16.1
Black Creek field	5856.1	+15.8

Note: CDT: Canyon Diablo troilite standard

(Carpenter et al., 1974; Hanor, 1979; Kharaka et al., 1987). Nevertheless, we have documented that intense thermochemical reduction of solid sulfate has taken place within the Smackover Formation in the deep part of the Mississippi salt basin at temperatures between 150 and 200 °C. The burial history (temperature--depth) curve of the Smackover Formation in the deep part of the Mississippi salt basin indicates that the formation has been subjected to temperatures of over 150 °C for more than 50 m.y. (Chapter 4). The replacement of anhydrite by calcite documented in this study suggests that the slow rate of reaction at these temperatures is sufficient for significant thermochemical reduction of solid sulfates over geological time supporting experimental studies by Orr (1982). Although solid sulfate appears unaltered in Smackover reservoirs at temperatures below 150 °C (Fig. 5), occurrences of high concentrations of hydrogen sulfide in these reservoirs (Orr, 1977) suggest that thermochemical reduction of dissolved sulfate has occurred at lower temperatures.

CONCLUSIONS

Pre-hydrocarbon migration diagenesis of the Smackover Formation is characterized by successive precipitation of calcite, saddle dolomite, and late anhydrite. Post-hydrocarbon migration diagenesis is dominated by replacement of previously formed late anhydrite by calcite or calcite

plus elemental sulfur and precipitation of post-bitumen calcite cement. The replacement of anhydrite by calcite is observed only in wells with formation temperatures greater than 150 °C, suggesting a thermochemical origin for this process. This replacement indicates that thermochemical reduction of solid sulfates can occur at temperatures as low as 150 °C at reasonable rates over geologic time.

ACKNOWLEDGMENTS

Supported by the Department of Geology, Applied Carbonate Research Program, and Basin Research Institute of the Louisiana State University. Discussions with R. Sassen were helpful during the course of this study. We also thank J. S. Hanor, R. Sassen, L. S. Land, R. D. Snelling, W. J. Wade, B. Carter, B. Kirkland, J. Banner, and A. Drew for reviews and comments. K. A. Mertz and F. T. Mackenzie reviewed the manuscript for Geology, and we thank them for their constructive comments.

REFERENCES CITED

- Anisimov, L. A., 1978, Conditions of abiogenic reduction of sulfates in oil-and-gas bearing basins: *Geochemistry International*, v. 15, p. 63-71.
- Carpenter, A. B., Trout, M. L., and Pickett, E. E., 1974, Preliminary report on the origin and chemical evolution of lead and zinc-rich oil field brines in central Mississippi: *Economic Geology*, v. 69, p. 1191-1206.
- Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I., 1980, The age curve of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations: *Chemical Geology*, v. 28, p. 199-260.
- Davis, J. B., and Kirkland, D. W., 1970, Native sulfur deposition in the Castile Formation, Culberson County, Texas: *Economic Geology*, v. 65, p. 107-121.
- 1979, Bioepigentic sulfur deposits: *Economic Geology*, v. 74, p. 462-468.
- Hanor, J. S., 1979, Sedimentary genesis of hydrothermal fluids, in Barnes, H.L., ed., *Geochemistry of hydrothermal ore deposits*: New York, John Wiley, p. 137-172.
- Heydari, E., and Moore, C. H., 1988, Oxygen isotope evolution of the Smackover pore waters, southeast Mississippi salt basin: *Geological Society of America Abstracts with program*, v. 20, p. A261.
- Hovland, M., Talbot, M. R., Qvale, H., Olaussen, S., and

- Aasberg, L., 1987, Methane-related carbonate cements in pockmarks of the North Sea: *Journal of Sedimentary Petrology*, v. 57, p. 881-892.
- Kharaka, Y. K., Maest, A. S., Carothers, W. W., Law, L. M., Lamothe, P. J., and Fries, T. L., 1987, Geochemistry of metal-rich brines from central Mississippi: *Applied Geochemistry*, v. 2, p. 543-561.
- Kirkland, D. W., and Evans, R., 1976, Origin of limestone buttes, Gypsum Plain, Culberson County, Texas: *American Association of Petroleum Geologists Bulletin*, v. 68, p. 2005-2018.
- Krouse, H. R., Viau, C. A., Eliuk, L. S., Ueda, A., and Halas, S., 1988, Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs: *Nature*, v. 333, p. 415-419.
- Machel, H. G., 1988, Some aspects of diagenetic sulfate-hydrocarbon redox reactions, in Marshall, J. D., ed., *Diagenesis of sedimentary sequences: Geological Society of London Special Publication 36*, p. 15-28.
- Meendsen, F. C., Moore, C. H., Heydari, E., and Sassen, R., 1987, Upper Jurassic depositional systems and hydrocarbon potential of southern Mississippi: *Gulf Coast Association of Geological Societies Transactions*, v. 37, p. 161-174.
- Moore, C. H., 1985, Upper Jurassic subsurface cements - a

- case history, in Schneidermann, N., and Harris, P. M., eds., Carbonate cements: Society of Economic Paleontologists and Mineralogists Special Publication 36, p. 291-308.
- Moore, C. H., and Druckman, Y., 1981, Burial diagenesis and porosity evolution, Upper Jurassic Smackover, Arkansas and Louisiana: American Association of Petroleum Geologists Bulletin, v. 65, p. 597-628.
- Orr, W. L., 1982, Rate and mechanism of non-microbial sulfate reduction: Geological Society of America, Abstract with Program, v. 14, p. 580.
- 1977, Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas, in Campos, R., and Goni, J., eds., Advances in organic geochemistry: Empresa Nacional Adaro de Investigaciones Mineras, v. 7, p. 571-597.
- 1974, Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation--study of Big Horn Paleozoic oils: American Association of Petroleum Geologists Bulletin, v. 58, p. 2295-2318.
- Parker, C. A., 1974, Geopressures and secondary porosity in the deep Smackover of Mississippi: Gulf Coast Association of Geological Societies Transactions, v. 24, p. 69-80.
- Pierre, C., and Rouch, J. M., 1988, Carbonate replacements after sulfates in the middle Miocene of Egypt: Journal

- of Sedimentary Petrology, v. 58, p. 446-456.
- Ritger, S., Carson, B., and Suess, E., 1987, Methane-derived authigenic carbonates formed by subduction induced pore-water expulsion along the Oregon/Washington margin: Geological Society of America Bulletin, v. 98, p. 147-156.
- Sassen, R., 1988, Geochemical and carbon isotopic studies of crude oil destruction, bitumen precipitation, and sulfate reduction in the deep Smackover Formation: Organic Geochemistry, v. 12, p. 351-361.
- Sassen, R., and Moore, C. H., 1988, Framework of hydrocarbon generation and destruction in eastern Smackover trend: American Association of Petroleum Geologists Bulletin, v. 72, p. 649-663.
- Sassen, R., Moore, C. H., Nunn, J. A., Meendsen, F. C., and Heydari, E., 1987, Geochemical studies of crude oil generation, migration, and destruction in the Mississippi salt basin: Gulf Coast Association of Geological Societies Transactions, v. 37, p. 217-224.
- Siebert, R. M., 1985, The origin of hydrogen sulfide, elemental sulfur, carbon dioxide, and nitrogen in reservoirs, in Sixth Annual Research Conference, Gulf Coast Section: Austin, Texas, Society of Economic Paleontologists and Mineralogists, p. 30-31.
- Trudinger, P. A., Chambers, L. A., and Smith, J. W., 1985, Low-temperature sulphate reduction: biological versus

abiological: Canadian Journal of Earth Sciences, v. 22,
p. 1910-1918.

Williams, C. H., Jr., 1969, Cross section from Mississippi-
Tennessee state line to Horns Island in Gulf of Mexico:
Jackson, Mississippi, Mississippi Geological Survey.

CHAPTER III

ASPECTS OF DIAGENESIS, GRAIN MINERALOGY, AND CALCITE CEMENT STRATIGRAPHY, UPPER SMACKOVER FORMATION, CLARKE COUNTY, MISSISSIPPI

ABSTRACT

The upper Smackover in Clarke County, Mississippi, exhibits a regional gradient in allochem mineralogy, dolomite content, and diagenetic alterations. Originally aragonitic grains and dolomite occur in the north, mixed aragonitic and calcitic grains with limited dolomite in the center, and calcitic grains and rare dolomite in the south. These features may have developed in response to regional variations in salinity and Mg/Ca ratio across the Smackover carbonate shelf, with hypersaline waters and high Mg/Ca ratio in the north and normal marine waters in the south. Intense early meteoric diagenesis with little burial overprint affected the northern area, moderate early meteoric and burial diagenesis in the center, and significant burial diagenesis and limited or no early meteoric diagenesis in the south.

Marine diagenesis is characterized by precipitation of fibrous and bladed isopachous calcite cements. Early pre-compaction features include extensive dissolution of originally aragonitic grains and precipitation of bladed isopachous and fine equant calcite cements both of which are non-luminescent to very dull luminescent.

Burial diagenesis consists of precipitation of zoned calcite cement, saddle dolomite, and anhydrite. The zoned calcite cements exhibit a similar sequence of luminescent zonation across the study area. However, intensity of

luminescence and number of zones vary across Clarke County. Nearly all zones postdate pressure solution features and rock fractures indicating that calcite cements precipitated late after significant burial.

The $\delta^{18}\text{O}$ values of younger zones are lower than older cement zones. The Sr isotopic values of younger zones are more radiogenic than the older zones. The $\delta^{13}\text{C}$ values of burial calcite cement zones and bulk calcite cements are similar to each other and to the host carbonate rock.

Petrographic observations and chemical compositions of zoned calcite cements suggest that cementation began after initiation of pressure solution by precipitation of very dull- to non-luminescent calcite cement zones across Clarke County. With further burial, fluid migration along faults imported Mn and radiogenic Sr which were incorporated in bright zones. Subsequent thermal maturation of kerogen resulted in release of H_2S which stabilized some Fe and Mn in to sulfides. As a result less of these elements were incorporated in the youngest dull zones.

The $\delta^{18}\text{O}$ and Sr isotopic signatures of calcite cements in East Nancy field suggest that the oxygen and Sr isotopic compositions of Smackover pore water has changed through time. The $\delta^{18}\text{O}$ and Sr isotopic values of the present day Smackover brines may have resulted from continuous interaction between original pore water and surrounding rocks. Further, the Smackover Formation may buffer the $\delta^{18}\text{O}$

and Sr isotopic compositions of pore waters in the Mississippi salt basin.

INTRODUCTION

The Smackover Formation is a marine unit of Oxfordian age (Imlay, 1980) deposited in and along the margins of a series of interior salt basins which rim the northern Gulf of Mexico. These basins formed as a result of early Mesozoic extension and opening of the main gulf (Wood and Wapler, 1974; Buffler and Sawyer, 1985). The basins are separated from each other and from the Gulf of Mexico by a series of physiographic and tectonic features. The Mississippi salt basin, encompassing most of southern Mississippi, is bounded on the west by the Monroe uplift, on the east by the Jackson graben, on the south by the Wiggins arch, and on the north by the Pickens-Gilbertown fault system (Fig. 3.1).

The Smackover Formation in Clarke County, Mississippi (Fig. 3.1), is dominantly limestone deposited on a narrow (50 km) carbonate shelf. It is buried from 2,700 m on the north to over 4,500 m in the southern part of the County. The Smackover Formation overlies siliciclastic deposits of the Norphlet Formation and is overlain by carbonates and evaporites of the Haynesville Formation (Fig. 3.2). Badon (1973, 1974) and Meendsen et al. (1987) reported details of stratigraphy, lithofacies, and depositional environments of this formation in Clarke County. Oglesby (1976) studied

Figure 3.1. Location map of Clarke County and other major physiographic features associated with the Mississippi salt basin.

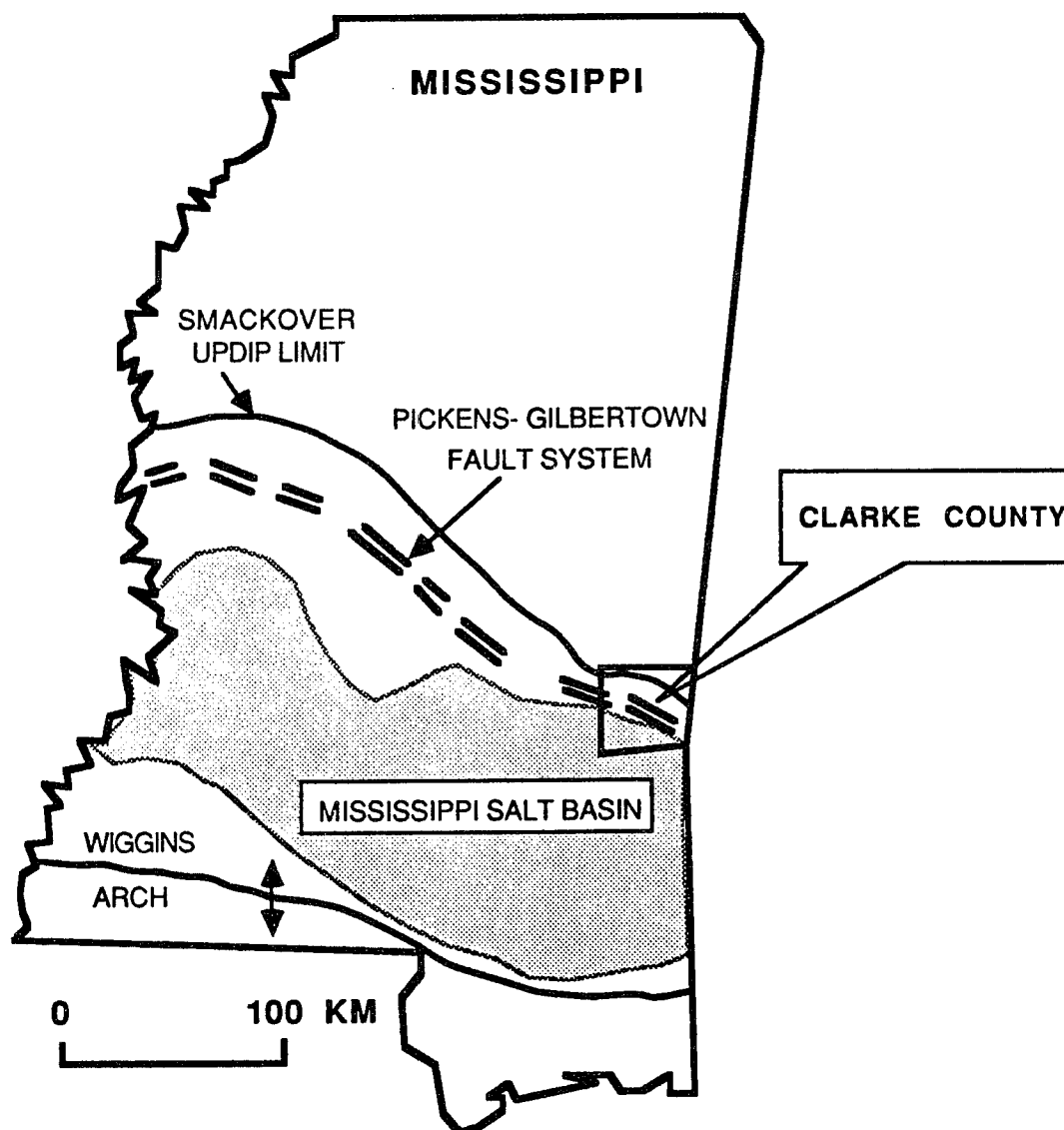


Figure 3.2. Simplified stratigraphic column showing Upper Jurassic formations in Clarke County (modified from Meendsen, 1987).

SERIES	STAGE	FORMATIONS	MEMBERS
LATE JURSSIC	TITHONIAN	SCHULER	
	KIMME- RIDGIAN	HAYNESVILLE	UPPER
			LOWER (BUCKNER EVAPORITE)
	OXFORDIAN	SMACKOVER	UPPER
			MIDDLE
			LOWER
		NORPHLET	
MIDDLE JURASSIC	CALLOVIAN	LOUANN	
		WERNER	
UPPER TRIASSIC		EAGLE MILLS	
PALEOZOIC BASEMENT			

cathodoluminescent behavior and trace element compositions of zoned calcite and dolomite cements in this area. He suggested that cementation of the upper Smackover Formation occurred shortly after deposition in a meteoric lens. Recent detailed diagenetic studies of the Smackover Formation in Louisiana and Arkansas (Moore and Druckman, 1981; Moore, 1985) cast doubt on Oglesby's interpretations. The present study was undertaken to investigate regional diagenesis of the upper Smackover Formation stressing petrographic characteristics, chemical composition, and variations in zonation of calcite cements in Clarke County. In addition, this study sheds light on effects of rock-water interaction on the origin and evolution of subsurface brines described from this area (Carpenter et al., 1974; Kharaka et al., 1987). Locations and names of the wells used in this study are presented in Figure 3.3. Cored intervals and bottom hole temperatures are given in Table 3.1.

ANALYTICAL METHODS

Petrographic observations were made on polished thin sections stained with alizarine red-s and potassium ferricyanide (Dickson, 1966). Cathodoluminescence (CL) observations were performed with a Technosyn luminescope. Operating conditions were 15 kv gun potential, focused beam diameter of about one centimeter, 0.5 millitor vacuum, and 300-400 μ A beam current.

Figure 3.3. Map of Clarke County showing the locations and names of the wells and fields referred in the text.

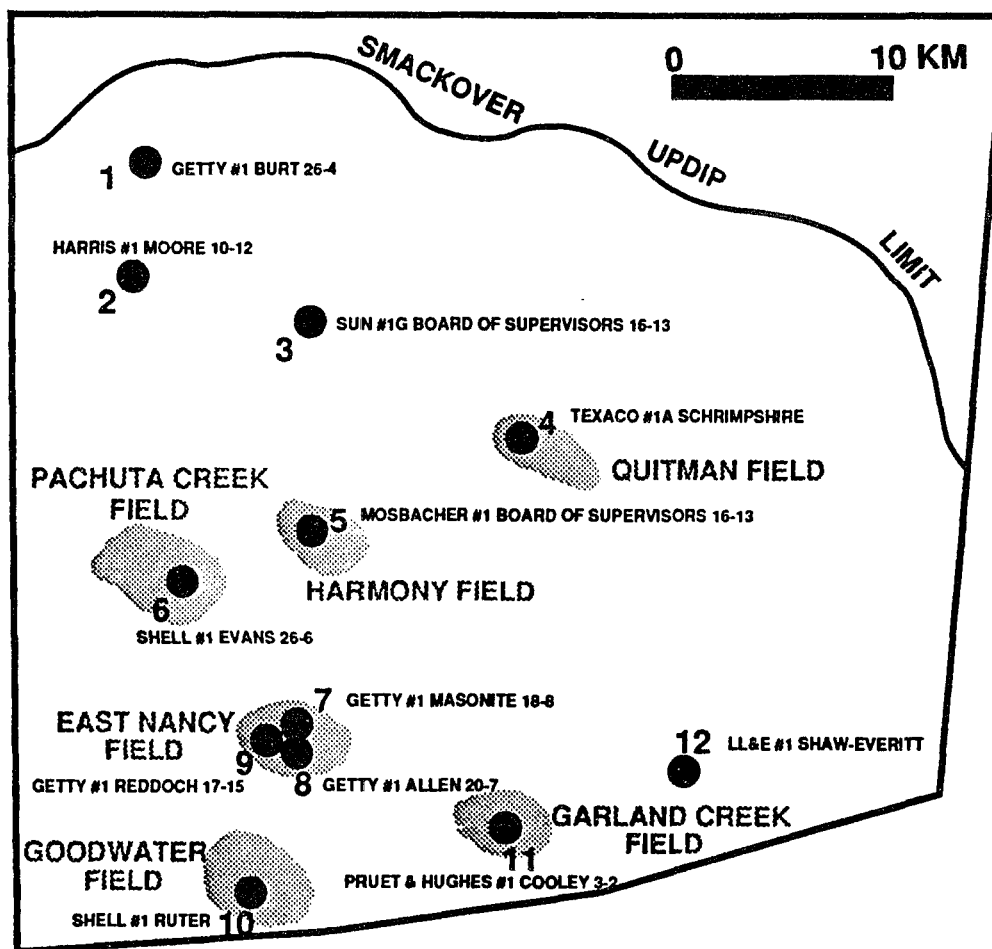


Table 3.1. Cores used in this study with bottom hole temperatures (uncorrected).

WELL NAME	CORE INTERVAL	T °C
1. Getty #1 Burt 26-4	10,206-10,216	82
2. Harris #1 Moore 10-12.	11,613-11,672	74
3. Sun #1 Board of Supervisors 16-13	10,711-10,801	82
4. Texaco #1A Schrimshire		
5. Mosbacher #1 Board of Supervisors 16-13	12,312-12,440	93
6. Shell #1 Evans 26-6	12,828-12,966	99
7. Getty #1 Masonite 18-8	13,509-13,672	100
8. Getty #1 Allen 20-7	13,525-13,642	104
9. Getty #1 Reddoch 17-15	13,531-13,558	90
	13,573-13,633	
	13,658-13,718	
10. Shell #1 Rutter	14,610-14,653	
11. Pruet & Hughes #1 Cooley 3-2	13,658-13,674	105
12. LL & E. Shaw-Everitt	13,393-14,915	99

Sampling of cements and allochems for chemical analyses was done by crushing the rock and separating cements and grains under a binocular microscope. Cement samples were stained slightly with alizarine red-s and handpicked a second time to avoid impurities. They were then washed with 0.05 N HCl to remove the stain and rinsed with distilled and deionized water three to five times. Separated samples were powdered in an agate mortar and pestle. The powdered samples were analyzed by X-ray diffraction from 20 to 32 degrees 2 θ to detect 100% reflection peaks of dolomite, anhydrite, calcite, celestite, and strontianite. Only mineralogically pure samples were chosen for chemical analyses.

For trace element analyses, 100 mg of a sample was dissolved in 0.5 N HCl. The leachate was passed through a 45 μ m millipore filter and its volume was raised to 100 mL. The analysis was performed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). The relative precision of analyses is 2.5% for Mg, 0.8% for Sr, 4.7% for Fe, and 7.9% for Mn. The detection limit for all elements is <1 ppm. Electron probe analyses were conducted with a JOEL 733 super probe with accelerating voltage of 15 kv, beam current of 30 na, and beam size of 20 μ m. Correction was done using a Bence-Albee scheme. Detection limits for Mg, Sr, Fe, and Mn were 500, 100, 300, and 200 ppm, respectively.

Oxygen and carbon isotopic analyses of carbonates were performed by Coastal Science Laboratories, Austin, Texas, by

reacting the carbonates with 100% orthophosphoric acid (McRea, 1950). The data are reported in ‰ and relative to PDB (Peedee Belemnite) standard with precision of ± 0.2 ‰. The $\delta^{18}\text{O}$ compositions of dolomites reported in this paper are not corrected for phosphoric acid fractionation (Sharma and Clayton, 1965). Strontium isotope analyses were performed by Dr. L. S. Land of the University of Texas at Austin. The Sr extraction was done by common ion exchange method. Precision of the analyses is ± 0.00005 .

DEPOSITIONAL SETTING

The regional depositional setting of the Smackover has been presented by Oxley et al. (1967), Dinkins (1968), Badon (1974), Moore (1984), Meendsen et al. (1987), and Eldridge (1988). The Smackover Formation in Clarke County is here divided into three members. The lower member directly overlies the Norphlet Formation and marks the initiation of Smackover transgression. It is approximately 10 m thick and is composed of an extremely well laminated mudstone. The laminations are crinkled and appear to be of algal origin. No other sedimentary features are observable, indicating deposition in a relatively deep, anoxic, and possibly hypersaline environment (Meendsen et al., 1987).

The middle member is 0 to 180 m thick and consists of alternating layers of laminated mudstone and burrowed mudstone and wackestone. Burrows in this member suggest that

the basin was becoming more oxygenated. Presence of beds containing rip-up clasts indicate that the basin was occasionally shallow enough that sediments were influenced by currents.

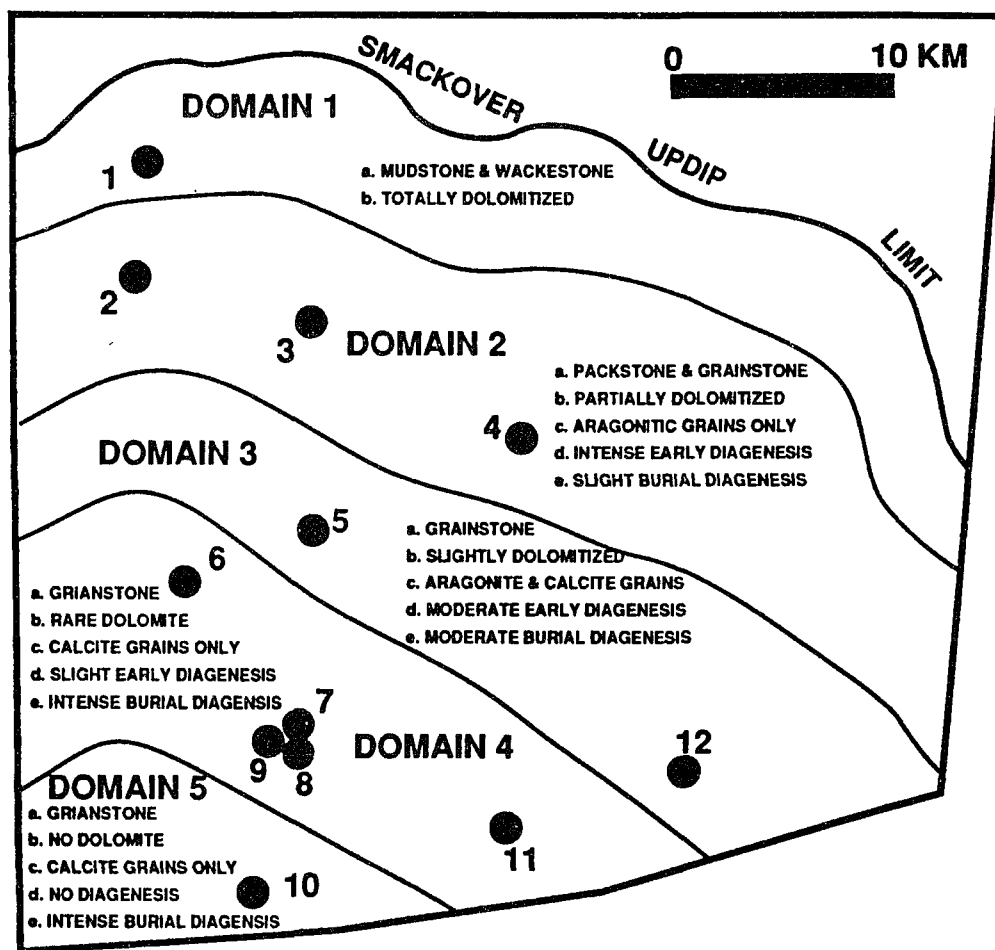
The upper member is composed of cross-laminated ooid dominated grainstones indicating deposition in a very shallow marine, high energy shoal complex (Meendsen et al., 1987). Deposition of this member records a sea level stand still or a small drop in sea level (Moore, 1984; Meendsen et al., 1987). The upper member is 0 to 180 m thick and is composed of several shoaling upward cycles.

Organic geochemical studies indicate that the lower and middle members are the source facies for the hydrocarbons in upper Smackover reservoirs (Oehler, 1984; Sassen et al., 1987a,b). The source facies is immature with respect to liquid hydrocarbons in the northernmost part of Clarke County, but it is within the oil window in the southern part of this area (Sassen and Moore, 1988).

LITHOFACIES OF THE UPPER SMACKOVER FORMATION

The upper Smackover Formation exhibits a north to south gradient in lithofacies in Clarke County. It is composed of totally dolomitized mudstone and wackestone in the northern most part of the county here termed domain 1 (Fig. 3.4). Southward in domain 2, it consists of highly dolomitized layers of packstone and grainstone with occasional interbeds

Figure 3.4. Depositional and diagenetic domains of the Smackover Formation, Clarke County. Well numbers per Figure 3.3 and Table 3.1.



of mudstone. Further south in domain 3 it is dominantly grainstone with limited dolomite. In the southern-most part of the county (domains 4 and 5) it is composed of oolitic grainstone. Thin dolomite beds occur at the tops of shoaling upward cycles in domain 4. These beds are not seen in domain 5. The mudstones and wackestones of the northern area have been interpreted as tidal flat sediments (Badon, 1974; Meendsen et al., 1987). The grainstones in the southern part of the county are thought to represent deposition on high energy shoals developed on top of salt structures (Badon, 1974; Meendsen et al., 1987).

An isopach map of the upper Smackover Formation (Fig. 3.5) shows that this member gradually thickens from its pinch-out in the northern part of Clarke County to over 180 m (600 ft) in the southern part of this area. A structure map drawn on the top of the Smackover Formation (Fig. 3.6) indicates that the formation dips gently southward. South of Pickens-Gilbertown fault system this trend is complicated by low to medium amplitude salt structures resulting from the movement of the Louann Salt (Hughes, 1976).

GRAIN TYPES OF THE UPPER SMACKOVER AND THEIR MINERALOGY

Previous studies of the upper Smackover in Louisiana and Arkansas (Becher and Moore, 1976; Brock and Moore, 1981, 1982; Moore and Druckman, 1981; Moore and Brock, 1982; Moore et al., 1986) have shown that factors such as grain types

Figure 3.5. Isopach map of the upper Smackover Formation in Clarke County. Thicknesses are in feet. Contour interval=100 ft. Well numbers per Figure 3.3.

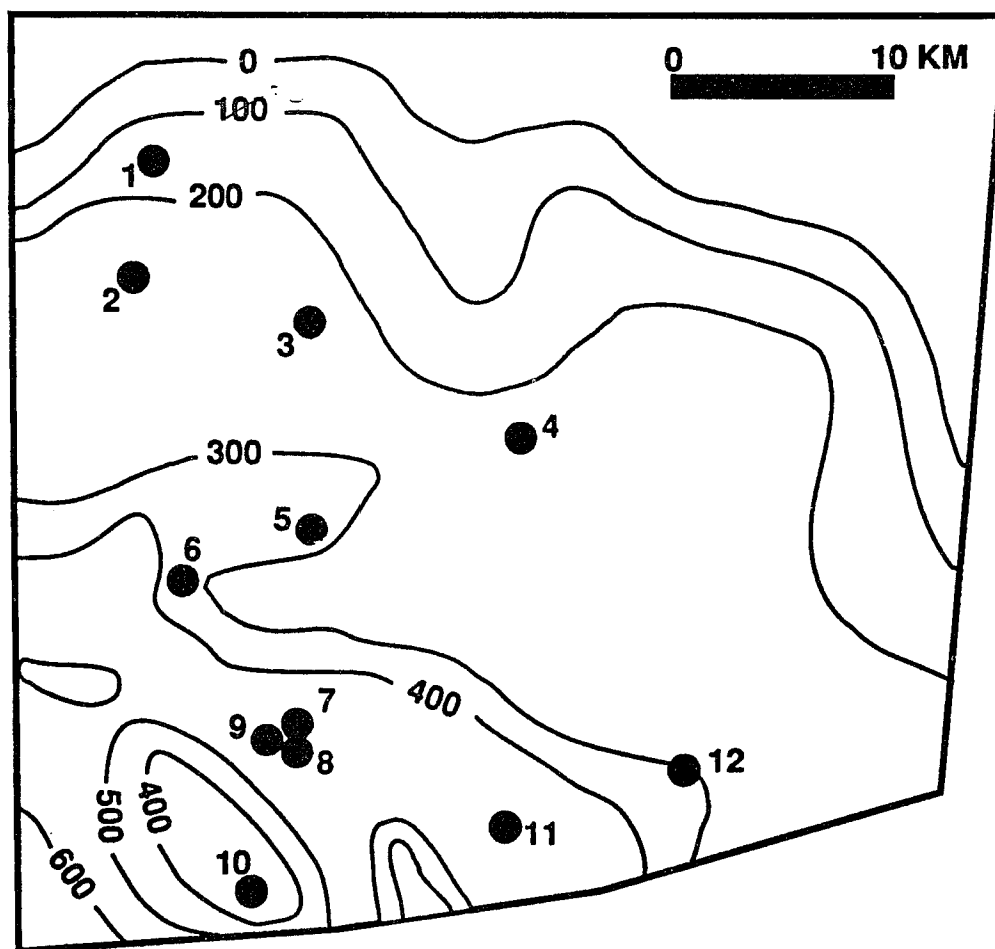
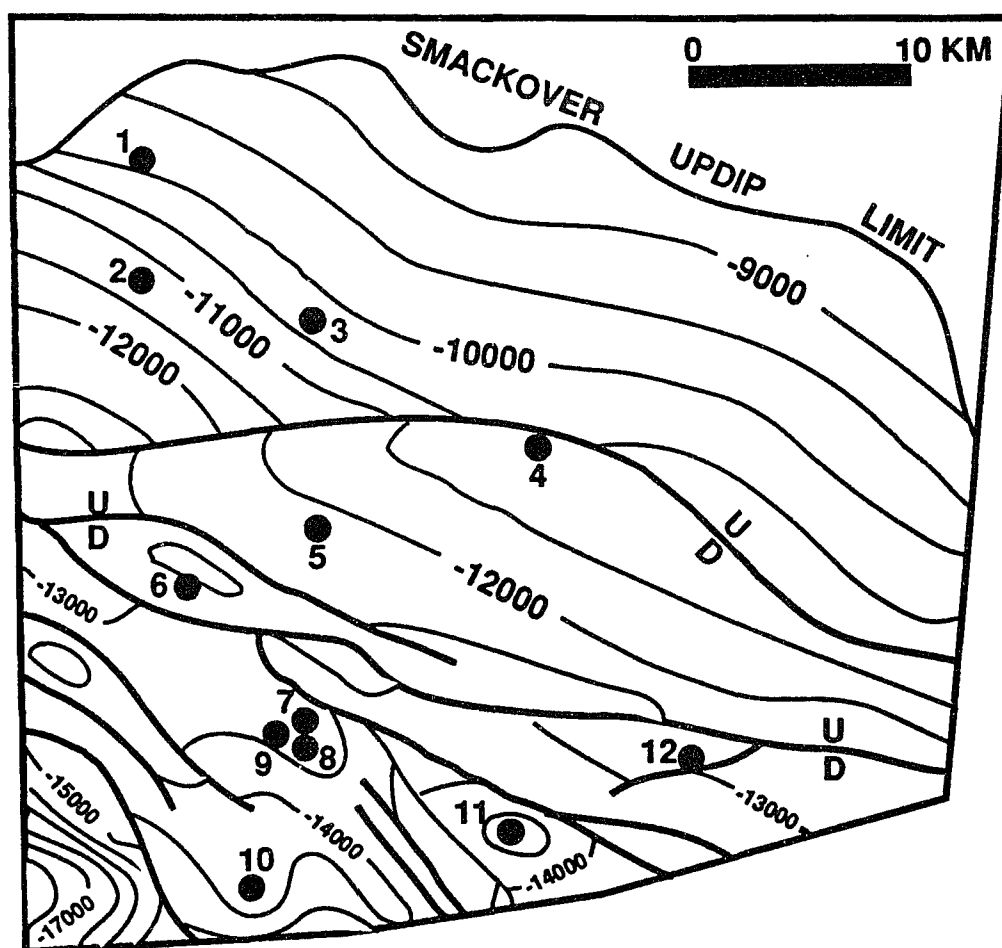


Figure 3.6. Structure drawn on the top of the Smackover Formation, Clarke County (Modified from Meendsen, 1987). Bold lines are faults. Well numbers per Figure 3.3. C. I. = 500 ft. D: Down thrown; U: Up thrown.



and their mineralogies have significant influence on the diagenesis of this formation. The upper Smackover grainstones in Clarke County are composed dominantly of ooids and algally coated grains. Red and green algae, corals, gastropods, and peloids comprise other minor allochems. Algal and coral boundstones are locally present and are previously described by Baria et al. (1982) and Crevello and Harris (1985).

Ooids

Petrographic and geochemical studies in Arkansas and Louisiana (Wilkinson et al., 1985; Moore et al., 1986; Swirydczuk, 1988) suggested that ooids there were originally composed of two mineralogical types: one aragonitic and the other calcitic. Similar features have been observed in Clarke County during the course of this study. The former calcitic ooids are presently composed of radial fabrics with concentric laminations. The former aragonitic grains are presently composed of neomorphosed mosaic of calcites, exhibit common moldic fabrics, and generally contain a concentric layers of neomorphosed calcite having a brick-like texture. Although these features are thought to be indicative of former aragonitic mineralogy the grains containing them can not always be clearly identified as ooids. Swirydczuk (1988) considered grains containing brick-like texture and molds as ooids. The origin of grains with

brick like texture is not clear. This texture was originally described by Assereto and Folk (1976) as an aragonite-to-calcite transformation of grains of algal origin from the Triassic. Grains with similar textures were interpreted as former aragonitic ooids from the Precambrian by Tucker (1985) and as former aragonitic pisoids from the Proterozoic by Swett and Knoll (1989). The grains containing brick-like textures in the upper Smackover Formation are significantly larger, generally less spherical, and commonly more irregular than calcitic ooids. It is not clear whether they were formed by physico-chemical precipitation or by biochemical processes. The large size of these grains indicate that they are probably not in hydraulic equilibrium with calcite ooids. Although their large size and irregular shape suggest that they may have been formed by algae, but no textural evidence is present to support their algal origin. If they are in fact abiotic they must have formed in an environment with very high salinity by rapid precipitation, and slow sedimentation rate to ensure their large size and irregular shapes. The molds could have been created by dissolution of aragonitic grains of any origin. It is possible that some of these molds were produced by dissolution of smaller algally coated grains and peloids. However, the fact that they show a uniform size and a circular cross section, suggests that some were ooids. The beds containing former aragonitic grains are significantly

lighter in color than the beds containing calcitic grains. More importantly, the originally aragonitic beds are less lithified than calcitic beds and occasionally crumble to loose grains. This is the opposite of what would be expected based on comparison to the differential lithification seen in other paired calcitic and aragonitic beds (James and Bone, 1989).

The inferred former aragonitic grains are most commonly found on the northern and landward margin of the Smackover carbonate shelf and the inferred calcitic ooids on the southern and basin ward part. This may suggest that these two ooids types were forming simultaneously on the same platform. However, Swirydczuk (1988) concluded the aragonitic ooids are older and occupied only the northern and landward part of the shelf in Arkansas and Louisiana. In Clarke County, originally aragonitic grains are present in the upper part of the upper Smackover in wells in domain 2, and underlie the calcitic ooid facies of the upper Smackover in wells in the central part of the platform in domain 3 (Fig. 3.4). Aragonitic grain facies have not been observed in the wells in domains 4 and 5 where all ooids are calcitic (Fig. 3.4). The aragonitic grains are either not present there or the section containing them has not been cored.

Algally Coated Grains

Types, origins, and nature of algally coated grains

require a separate and detailed study. Several kinds of microtextures are observed in these grains which indicate that different species of algae may have been responsible for their formation (see Peryt, 1983). Algally coated grains range in sizes from 1 to 50 mm in diameter and can be mistaken for ooids when small (<2 mm). In general, they are larger, less spherical, and more irregular than ooids. They show various textures depending on type of algae and energy of the environment (Becher and Moore, 1976). Those in the lower part of the upper Smackover are very irregular and their cortex is composed of loosely bound grains. Those in the upper part of this member are more spherical. Their cortex does not exhibit a binding texture but rather is composed of nearly concentric layers with radial or micritic textures suggesting that they were formed by calcifying algae.

Original mineralogies of the algally coated grains may have paralleled that of ooids. Microtextural details of algally coated grains are very well preserved in the southern-most part of area in domains 4 and 5 (Fig. 3.4) suggesting that, like the ooids in the area, the algal grains were also originally calcitic. Further north in domain 3, originally calcitic algally coated grains are present. If grains containing brick-like textures were of algal origin, then this domain contains bi-minerallic algally coated grains as well as ooids. The few algally

coated grains that are present in domain 2 show brick-like textures suggesting that they were probably originally aragonitic.

Cause of the Regional Gradients

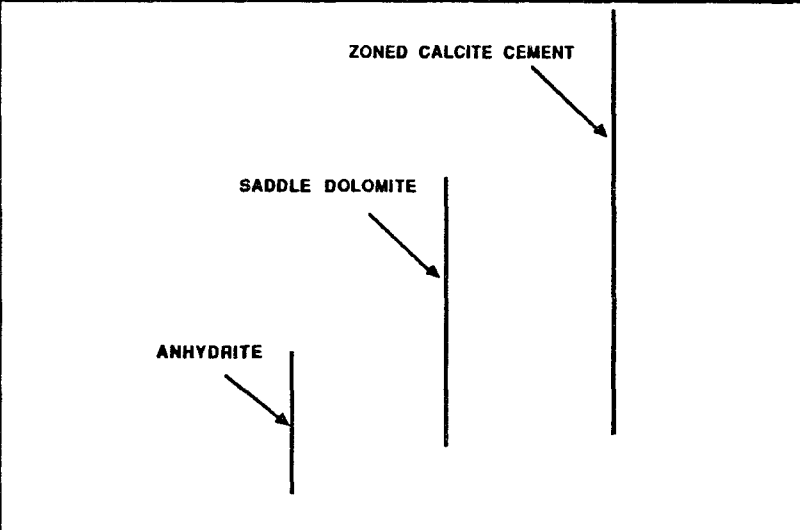
The regional variation in dolomitization and grain mineralogies described above can be reasonably explained by a platform-wide gradient in water salinity and Mg/Ca ratio across Clarke County. Evaporative conditions in the north resulted in highly saline waters with very high Mg/Ca ratio which favored syndepositional dolomitization in domain 1 and formation of aragonite-dominated allochems in domain 2. This is consistent with the formation of only aragonitic components in modern lakes with very high Mg/Ca ratio (Hardie, 1987). Lack of significant early dolomite and the dominance of calcitic grains in domains 4 and 5 indicate normal marine conditions. This is consistent with the conclusions of Sandberg (1983) who inferred that sea water composition and a much higher atmospheric partial pressure of CO₂ during the upper Jurassic favored precipitation of calcite. The presence of mixed aragonitic and calcitic allochems and limited dolomite in domain 3 indicate that this area was a transition zone between an evaporative environment to the north and normal marine conditions to the south.

EARLY DIAGENESIS

Early diagenetic processes include marine cementation, syndepositional dolomitization, and post depositional dissolution and cementation. Marine cements are fibrous and bladed isopachous calcite. Micritic cements fill pores of some grainstones. The fact that these samples are coarse-grained, well sorted, and cross-bedded indicate that the micrite is cement rather than detrital mud. In addition, petrographic characteristic of these micrites are similar to those described by Moore (1973) and interpreted by him as such.

The regional variation in occurrence of dolomite, grain mineralogies, as a function of distance from the paleoshore line has caused systematic differences in early post-depositional dissolution, cementation, and porosity types from north to south across Clarke County (Fig. 3.7). The Smackover Formation in domain 1 (Fig. 3.4), where early dolomitization was common, contains dolomitic intercrystalline and moldic porosities. In domain 2, where grains were originally aragonitic, extensive dissolution has created moldic porosity and provided calcium carbonate for bladed and fine equant calcite cements. In domain 3 (Fig. 3.4), where both originally calcitic and aragonitic grains were present, moldic, intercrystalline, and intergranular porosities are seen. In domain 4, where all grains were originally calcitic, only minor dissolution is observed and

Figure 3.7. Paragenetic sequences for the upper Smackover Formation in four domains in Clarke County.

MINERAL EMPLACEMENT AND DISSOLUTION						COMPACTIONAL PROCESSES	
EARLY DIAGENESIS	DOMAIN 5	DOMAIN 4	DOMAIN 3	DOMAIN 2	DOMAIN 1		
	NO DOLOMITIZATION	RARE DOLOMITIZATION	LIMITED DOLOMITIZATION	INTENSE DOLOMITIZATION	INTENSE DOLOMITIZATION		
	NO DISSOLUTION	RARE DISSOLUTION	LIMITED DISSOLUTION	INTENSE DISSOLUTION	INTENSE DISSOLUTION		
	NO CEMENTATION	RARE CEMENTATION	LIMITED CEMENTAION	INTENSE CEMENTATION	RARE CEMENTATION		
BURIAL DIAGENESIS					RARE BURIAL CEMENTATION	GRAIN DEFORMATION	TIME (DEPTH OF BURIAL) ↓
						GRAIN-TO-GRAIN PRESSURE SOLUTIONING	
						STYLOLITIZATION	
						AND ROCK	
	HYDROCARBON MIGRATION				NO HYDROCARBON MIGRATION	FRACTURING	
	HYDROCARBON DESTRUCTION AND SOLID BITUMEN PRECIPITATION						

that only in exposure surfaces capping shoaling upward cycles. In domain 5 grains were calcitic and no early dissolution was observed. Early cementation in domains 4 and 5, other than marine cement, is very rare. The lack of cement is a function of an absence of a source of elevated levels of dissolved calcium carbonate because allochems are dominantly calcitic. Stabilization of high Mg-calcitic to low Mg-calcite consumes Ca rather than producing it. James and Bone (1989) showed that sediments composed of calcite grains exposed to intense meteoric diagenesis for 10 m.y. are still uncemented. Primary intergranular porosity is the only significant porosity type in these domains.

Extensive dissolution of aragonitic allochems in domains 1 and 2 suggests that the upper Smackover Formation was exposed to undersaturated waters shortly after deposition in this area. The nature of water causing the dissolution is difficult to determine. It may have been fresh meteoric or evaporative-concentrated meteoric brine. Two samples containing early cements from this area show very heavy oxygen and carbon isotopic values. Light carbon isotopes indicative of meteoric calcites (Lohmann, 1987; Carpenter et al., 1988) have not yet been found. This could be due to a lack of a well developed soil zone or other significant organic material in an arid environment or insufficient data. No evidence exists for dissolution or meteoric influence in domain 5 and limited dissolution is

observed in domain 4. This indicates that pore waters may have remained normal marine in this area. Presence of moldic porosity in domain 3 suggests that dissolution occurred in this area and the pore water might have been transitional between a meteoric dominated system in the north to a marine dominated system in the south. This is similar to the regional pore water variation pattern inferred by Moore and Druckman (1981) and Moore (1985) for the Smackover Formation in Arkansas and Louisiana.

BURIAL DIAGENESIS

The regional pattern of dolomitization, grain mineralogies, and early diagenesis has resulted in the development of a regional gradient in the intensity of burial diagenesis across Clarke County. Burial features, including physical and chemical compaction and cementation, are generally rare in domains 1, rare to common in domain 2, common in domain 3, and intense in domains 4 and 5. However, the sequence of burial cementation is similar across the area despite mineralogical and early diagenetic differences (Fig. 3.7). Burial events are dominated by the precipitation of a zoned pore-fill calcite cement followed by saddle dolomite and late anhydrite (Fig. 3.7). Quartz overgrowths, silica replacement of allochems, and kaolinite cements are subsidiary phases of the sequence.

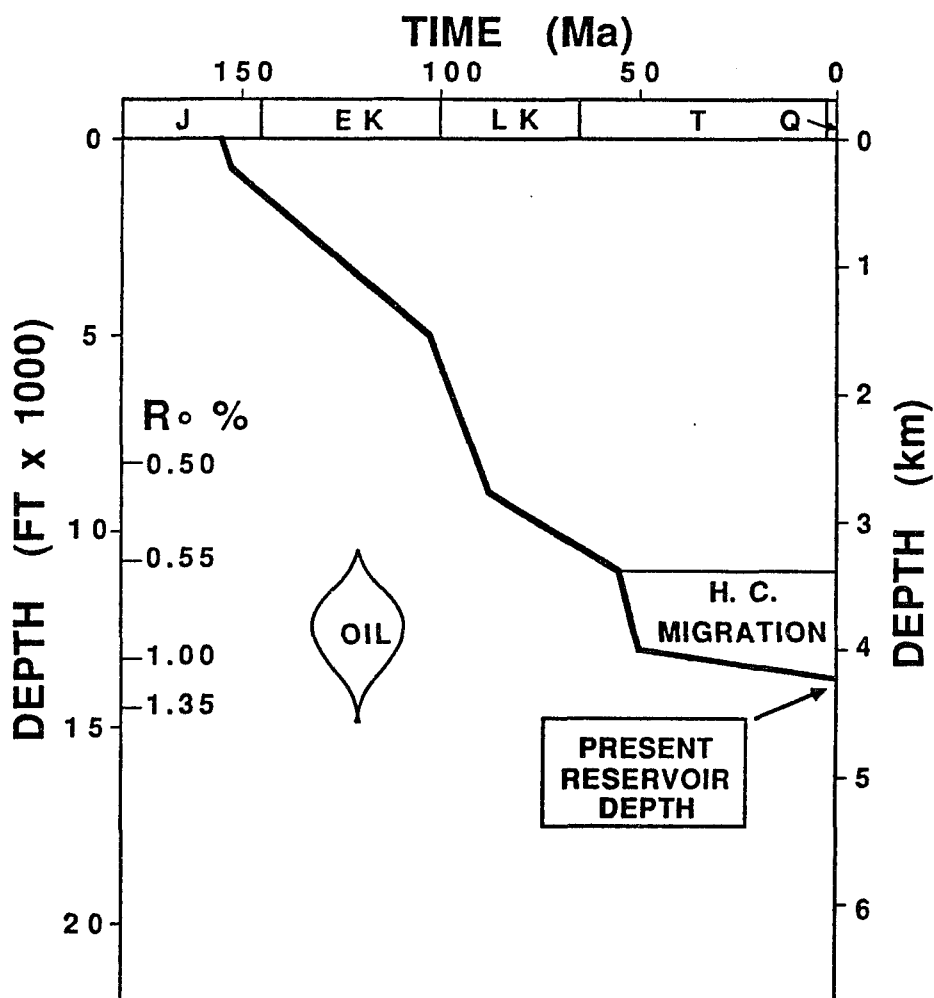
The burial (time-temperature) history of the Smackover

Formation in East Nancy field (Fig. 3.8) reveals that hydrocarbon generation and migration (vitrinite reflectance of 5.5, Sassen et al., 1987b) occurred at about 3,355 m of burial in the Early Tertiary, and ended at (vitrinite reflectance of 1.35, Sassen et al., 1987b) about 4,270 m of burial in the middle Tertiary. Hydrocarbon migration in reservoirs locally ended precipitation of inorganic cements. Thermal maturation and cracking of liquid hydrocarbons in the southern part of Clarke County in domains 4 and 5 resulted in the precipitation of solid bitumen.

Calcite Cement

Calcite cementation is the most common burial diagenetic event in the Smackover Formation in Clarke County. With the exception of the Sun #1G Board of supervisors 16-13 well (Fig. 3.3), all calcite cements are Fe poor and do not reveal zonation when stained with alizarin red-S and potassium ferricyanide. However, all calcite cements show zonation when viewed with a luminescope. Intensity and color of luminescence and number of zones are variable in samples from different localities across the carbonate shelf. For this reason the CL zonation of calcite cements from each location is described separately, starting with the most shoreward wells and progressing basinward.

Figure 3.8. Burial history curve of the top of the Smackover Formation reconstructed from the compacted thicknesses of sediments from the Getty #1 Masonite 18-8 well in East Nancy field. Vitrinite reflectance (R_0) data are estimated from calculated time temperature indices (Waples, 1980).



Sun #1G Board of Supervisors 16-13

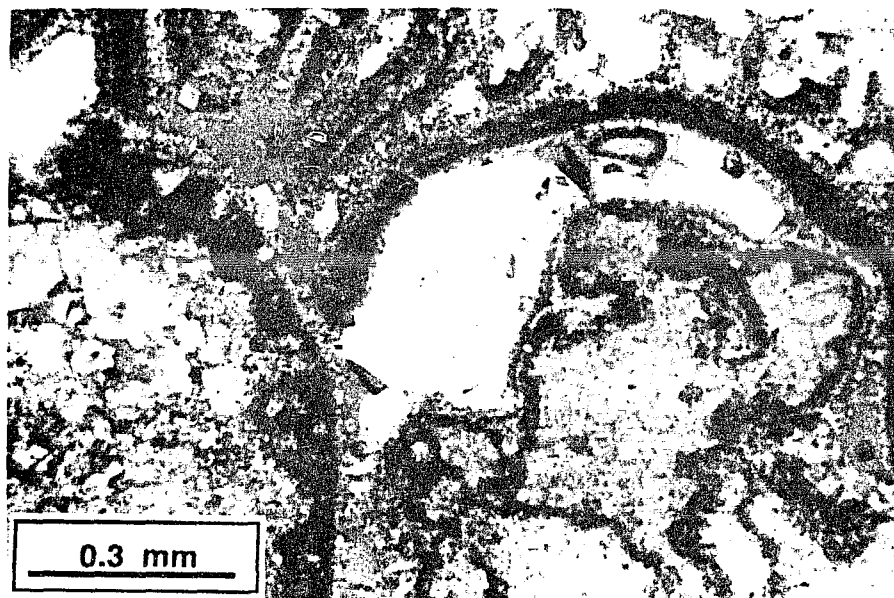
Burial calcite cementation in this well (well 3, Figs. 3-6) is uncommon due to the strong early diagenetic overprint characteristic of this area. When present, burial cements are ferroan and reveal zonation when stained. In addition, they exhibit four zones when viewed with the luminescope (Fig. 3.9). These zones from older to youngest are very dull-luminescent zone 1 (dark brown), dull luminescent zone 2 (brown), very bright luminescent zone 3 (yellow), and moderately bright luminescent zone 4 (orange) (Fig. 3.9). Petrographic observations indicate that these cements are post-compaction. For instance, zones 3-4 fill stylolite related extension fractures (Fig. 3.10).

Four samples of zones 3 and 4 calcites have $\delta^{18}\text{O}$ compositions ranging from -6.7 to -7.9 with an average of -7.2. Their $\delta^{13}\text{C}$ composition ranges from +3.9 to +4.6 with an average of +4.1. The samples contain an average of 2214 ppm Mg, 126 ppm Sr, 494 ppm Fe, and 646 ppm Mn. Their Sr isotopic composition ranges from 0.70802 to 0.70813 with an average of 0.70809 (Table 3.2).

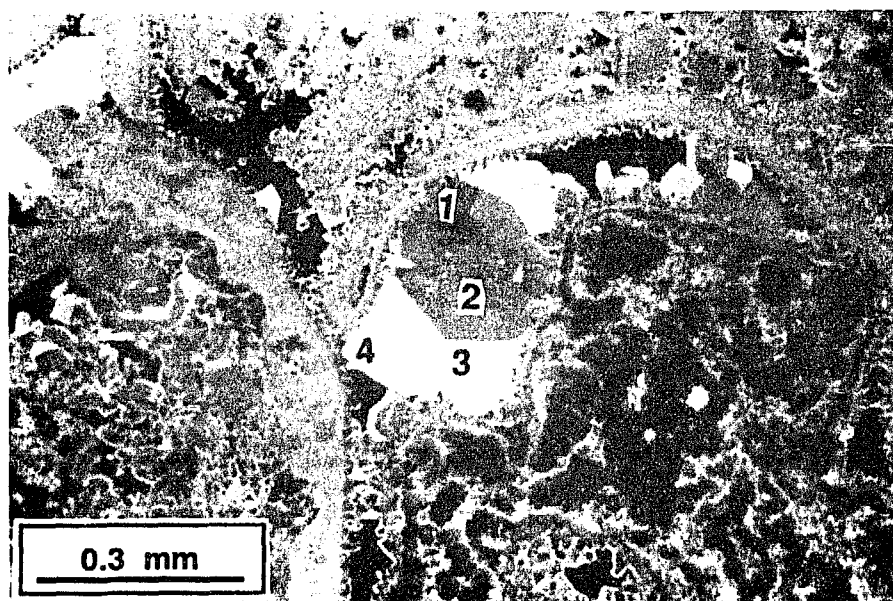
Harmony Field

Calcite cements from Mosbacher #1 Board of Supervisors well (well 5, Figs. 3-6) also exhibit four zones. However, all zones have dull luminescent intensities when compared to cements from the Sun #1 Board of Supervisors 16-13 well to

Figure 3.9. (A) Plain light and (B) Cathodoluminescence (CL) photomicrographs of zoned calcite cements showing four zones. Sun #1G Board of Supervisors 16-13, 3,279 m.

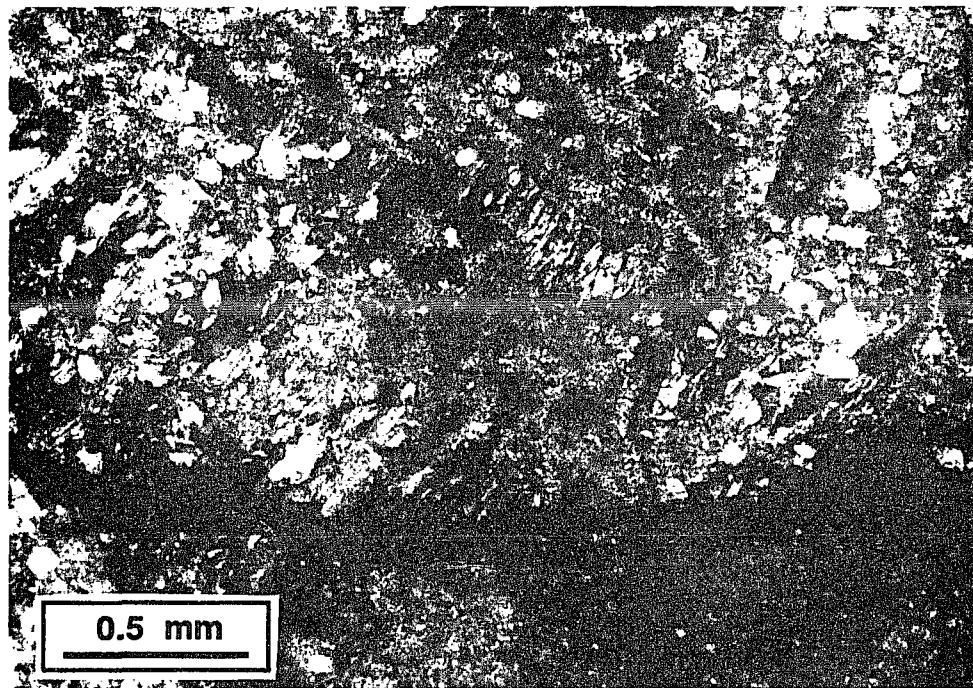


A

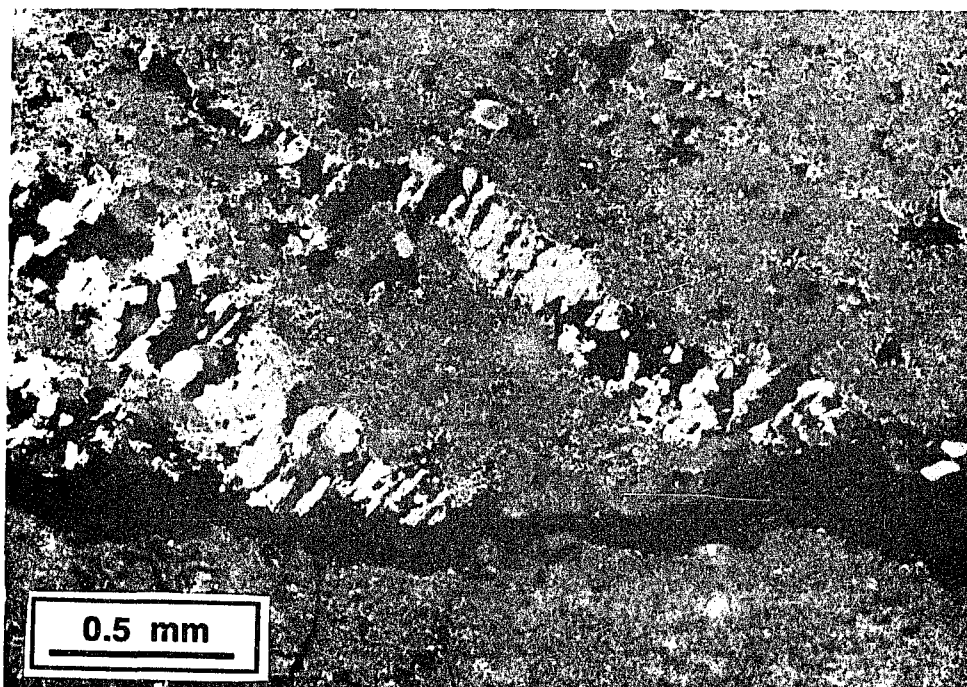


B

Figure 3.10. (A) Plain light and (B) CL photomicrographs of cement zones 3-4 filling late stylolite-related fractures. Sun #1G Board of Supervisors 16-13, 3,288 m.



A



B

Table 3.2. Trace elements and oxygen, carbon, and strontium isotopic compositions of calcite and saddle dolomite cements. Trace elements in ppm; oxygen and carbon isotopes in o/oo relative to PDB.

Depth(m)	Mg	Sr	Fe	Mn	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$87\text{Sr}/86\text{Sr}$
<u>Sun #1 Board of Supervisors</u>							
Zones 3-4							
3,273	1327	92	239	393	-6.7	+4.6	0.70802
3,284	3575	180	716	731	-7.9	+3.8	0.70813
3,287	2740	107	526	794	-7.6	+4.0	0.70813
3,288					-7.1	+3.9	
Saddle Dolomite							
3,291		68	11693	372	-4.6	+5.2	
3,291		59	10978	408	-5.1	+5.2	
<u>Getty #1 Reddoch (East Nancy Field)</u>							
Bulk Cement							
4,128	2884	89	DL	26	-5.8	+4.1	
4,175	2580	121	DL	34	-5.9	+4.5	
Zones 1-2							
4,129	2196	97	00	30	-5.6	+4.5	0.70727
4,130	2144	89	00	29	-6.0	+4.7	0.70721

Zones 3-4

4,176	120	00	332	-8.4	+4.6	0.70856
4,169	95	00	318	-8.0	+4.6	0.70823

Shell #1 Rutter (Goodwater Field)**Bulk Cement**

4,764	2959	87	DL	26	-5.1	+4.3
4,765	2579	99	DL	26	-5.6	+4.0
4,765	2458	126	DL	26	-5.7	+4.0

the north and Shell #1 Evans 26-6 well to the south. Zone 1 is non-luminescent (black) and the other three zones are all dull to very dull luminescent (light to dark brown) (Fig. 3.11). Cementation postdates compaction and pressure solution (Fig. 3.11).

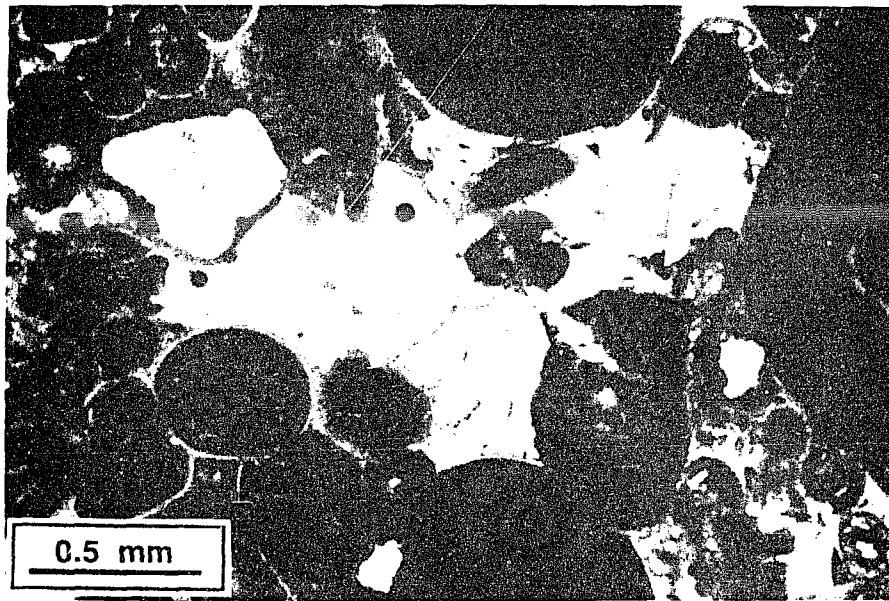
No chemical analyses of these cements are available at this time. However, four samples of calcitic ooids from this well have $\delta^{18}\text{O}$ compositions ranging from -0.7 to -2.9 with an average of -1.8. Their $\delta^{13}\text{C}$ ranges from +4.0 to +4.3 with an average of +4.2. These oolite samples are from the uppermost oolitic section of the well. Note that $\delta^{18}\text{O}$ becomes significantly lower with depth. The $\delta^{13}\text{C}$, however, is neither low nor variable. The same samples contain an average of 5707 ppm Mg, 261 ppm Sr, 134 ppm Fe, and 31 ppm Mn (Table 3.3).

Pachuta Creek Field

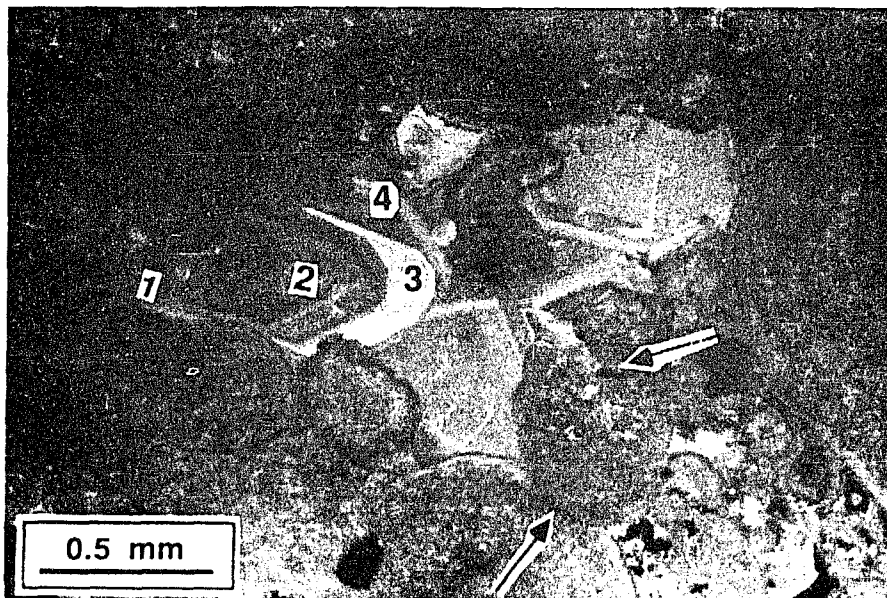
The Shell #1 Evans 26-6 well (well #6, Figs. 3-6) was analyzed in detail from this field. Cements from this well were previously studied by Oglesby (1976). Based on CL characteristics, Oglesby (1976) recognized as many as nine zones in the calcite cements. However, the results of the present study show that all of Oglesby's zones can be grouped into 5 easily recognizable zones (Fig. 3.12). The sequence of zones is: (1) very dull luminescent zone 1 (dark brown), (2) dull luminescent zone 2 (brown), (3) moderately

Figure 3.11. (A) Plain light and (B) CL photomicrographs of zoned calcite cement showing four zones. Cements postdate grain fracturing and grain-to-grain pressure solution.

Mosbacher #1 Board of supervisors 16-13, 3,803 m.



A



B

Table 3.3. Trace elements and oxygen, carbon, and strontium isotopic compositions of the Smackover calcite ooids. Trace elements in PPM. Carbon and oxygen isotopes in o/oo relative to PDB.

Depth(m)	Mg	Sr	Fe	Mn	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$87\text{Sr}/86\text{Sr}$
----------	----	----	----	----	-----------------------	-----------------------	---------------------------

Mosbacher #1 B. of Supervisors (Harmony Field)

3,770	4874	302	95	29	-0.7	+4.3	
3,771	7484	236	37	29	-1.6	+4.1	
3,773		258	281	32	-2.1	+4.0	
3,774	4764	249	123	33	-2.9	+4.4	

Shell #1 Evans (Pachuta Creek Field)

3,916	3056	346	9	46	-2.9	+4.4	
3,941	3875	312	DL	38	-1.6	+4.1	
3,943	3911	273	86	31	-1.5	+3.9	

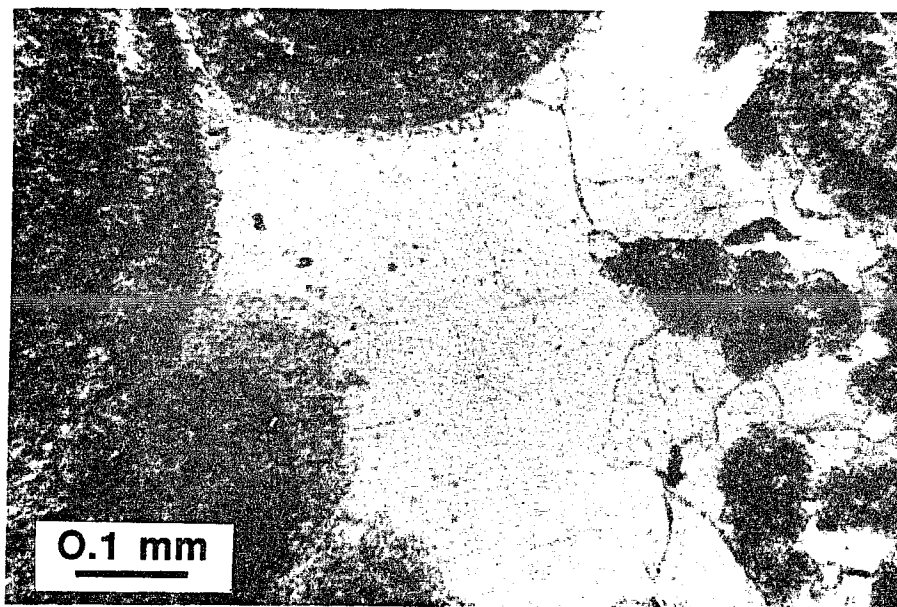
Getty #1 Allen 20-7 (East Nancy Field)

4,125	3559	456	121	31	-3.1	+4.0	
4,127	4100	477	128	34	-3.4	+3.8	0.70690
4,128	3169	273	89	44	-2.7	+4.4	0.70697
4,130	----	281	66	35	-2.5	+4.6	

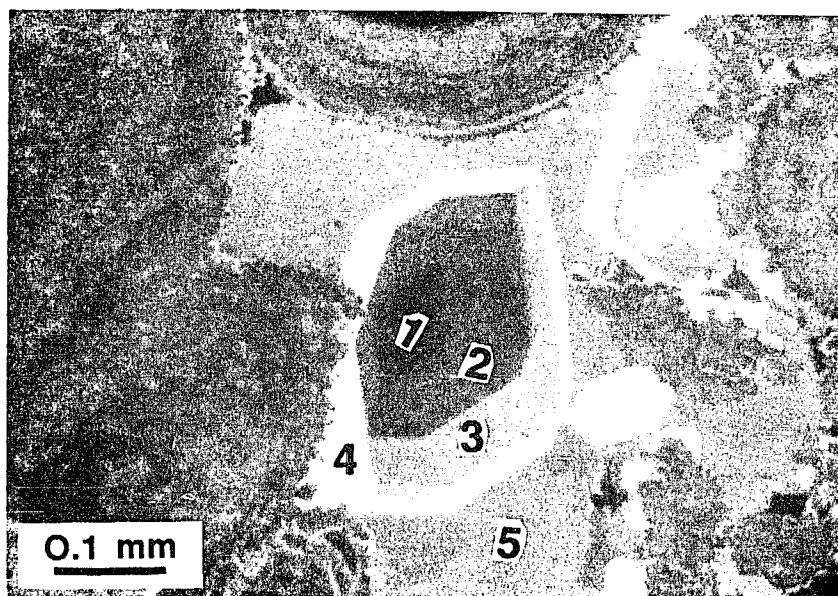
Shell #1 Ruter (Goodwater Field)

4,761	4491	217	DL	14	-2.4	+4.4
4,763	4696	251	DL	13	-2.8	+4.3
4,764	3051	289	DL	11	-3.0	+4.3

Figure 3.12. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing five zones. Shell #1 Evans 26-6, 3,941 m.



A



B

bright luminescent zone 3 (orange), (4) very bright luminescent zone 4 (yellow), and (5) moderately bright luminescent zone 5 (orange). Zones 1-3 of this study correspond very well with zones 1-3 of Oglesby (1976). Zone 4 in some cements exhibits several thin sub-zones with very similar luminescent intensities. For simplicity all are grouped as zone 4 in the present study. Oglesby (1976), however, counted each sub-zone separately. Zone 4 of the present study correlates with his zone 4 in some cements and to his zones 4-8 in those calcites where the sub-zones are present. Zone 5 of the present study correlates fairly well with Oglesby's zone 5 when subzones are not present.

Based on the luminescent character and Fe, Mn, and Mg contents of cement zones, Oglesby (1976) proposed the following conditions of precipitation for each zone. Very dull luminescent zone 1 (stage one cement generation) precipitated from an oxygenated meteoric water. Dull and moderately bright zones 2-3 (stage 2 cement generation) formed in an equal mixture of fresh-water and sea-water in a less oxygenated environment. Brightly luminescent zone 4 (stage 3 cement generation) precipitated from a reduced fresh-water-sea-water mixture, and finally, moderately bright luminescent zone 5 (stage 4 cement generation) was formed by a fresh water-sea water-hypersaline-water mixture in the presence of H_2S . Based on this model, all cement zones formed early within a meteoric lens prior to

compaction.

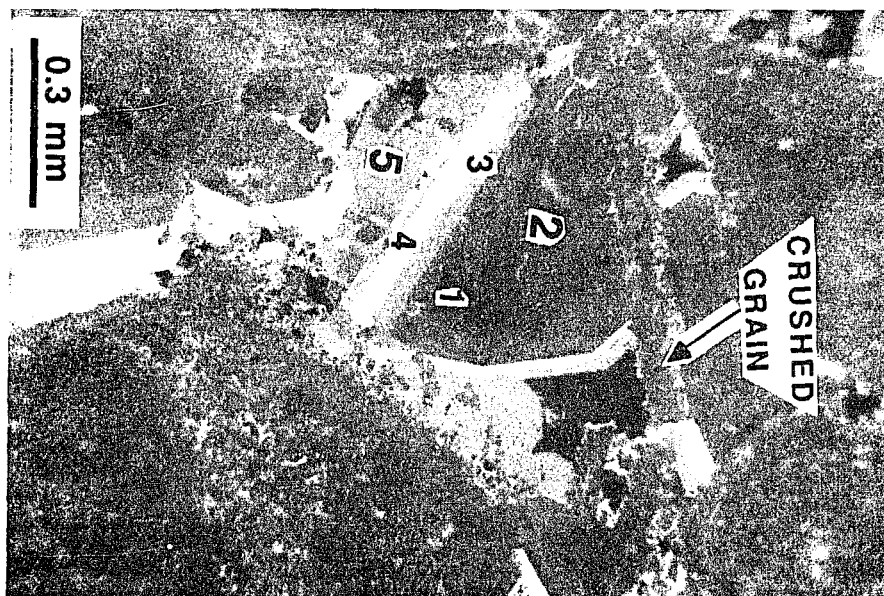
Petrographic observations strongly suggest that the majority, or all of zoned calcite cements from the Shell #1 Evans 26-6 well formed relatively late and after significant burial and compaction. Zone 1 was not seen to postdate any physical and chemical compaction features. Therefore, it is possible that zone 1 is an early pre-compaction cement. Zone 1 commonly exhibits an irregular crystal boundary with zone 2 (Figs. 12, 13), also noted by Oglesby (1976). This irregular boundary was observed between zone 1 and the next younger zone in all zoned calcite cements in Clarke County. Similar relationships observed elsewhere have been ascribed to either dissolution of the crystal face by undersaturated water or to irregular crystal growth (Meyers, 1974; Searl, 1988). The irregular crystal boundaries studied do not resemble the dissolution features of calcite cement zones reported by Kaufman et al. (1988). Their origin is uncertain but it is doubtful that it was produced by corrosion in the presence of undersaturated solutions.

Zone 2 postdates grain deformation (Figs. 13 and 14, and Fig. 3.12 of Oglesby, 1976). In addition, small amounts of this zone occurs in late extensional fractures (Fig. 3.15). These fractures are apparently formed by a crack-seal mechanism (Ramsay, 1980) and are commonly associated with stylolites (Phillips, 1974; Fletcher and Pollard, 1981; Nelson, 1981). Such fractures in this study are dominantly

Figure 3.13. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing zone 2 cement postdates grain compaction. Shell #1 Evans 26-6, 3,941 m.

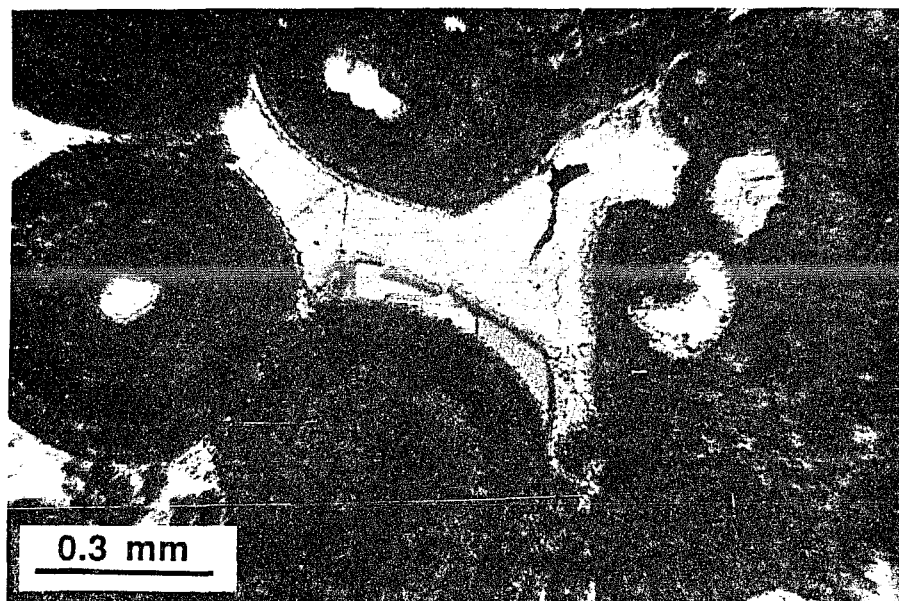


A

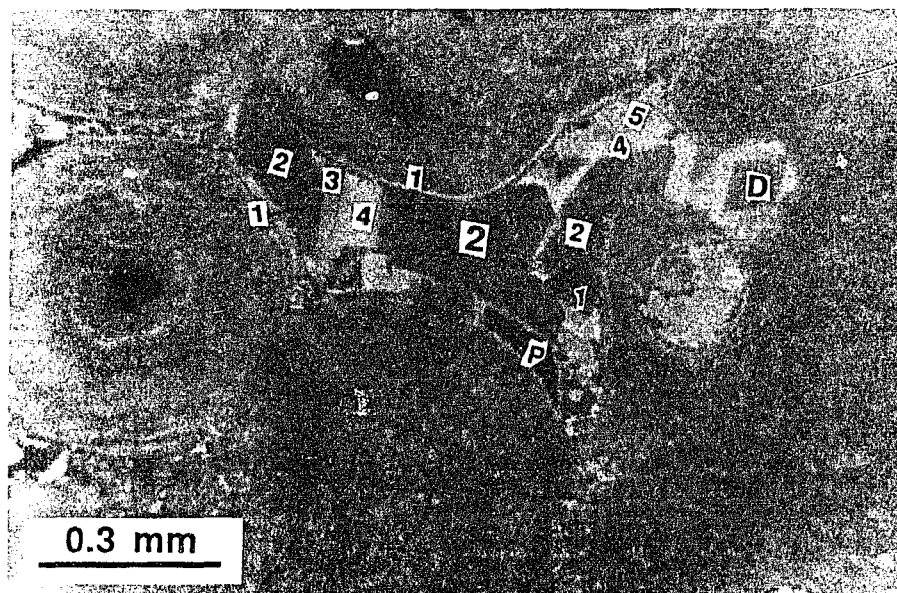


B

Figure 3.14. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing that zone 2 cement postdates spalled ooid. Shell #1 Evans 26-6, 3,941 m.



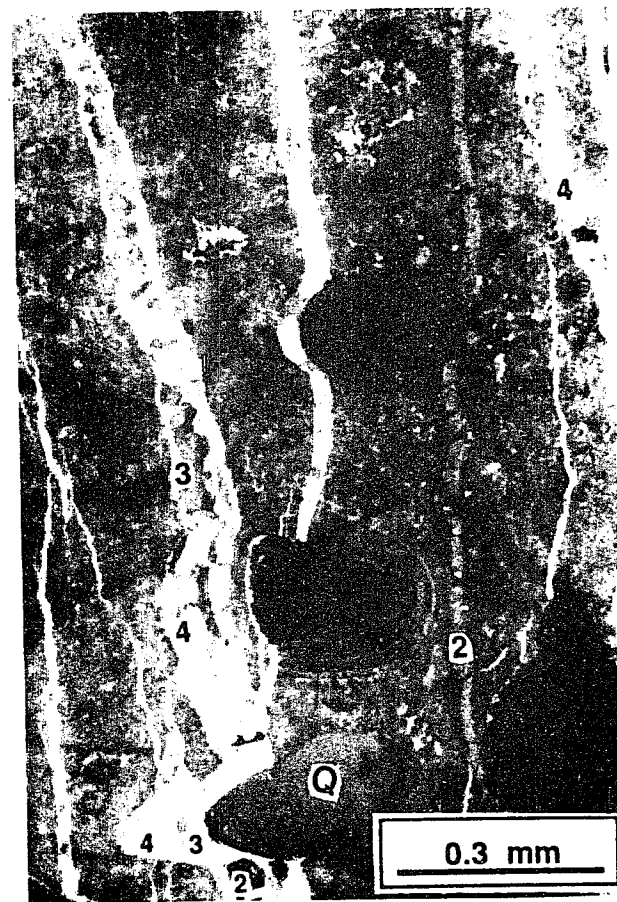
A



B

Figure 3.15. (A) Plain light and (B) CL photomicrographs of zoned cements filling late, stylolite related, extension fractures. Zone 2 cement is the oldest fracture fill indicating that this zone postdates stylolites and rock fractures. Shell #1 Evans 26-6, 3,944 m.

Figure 3.15



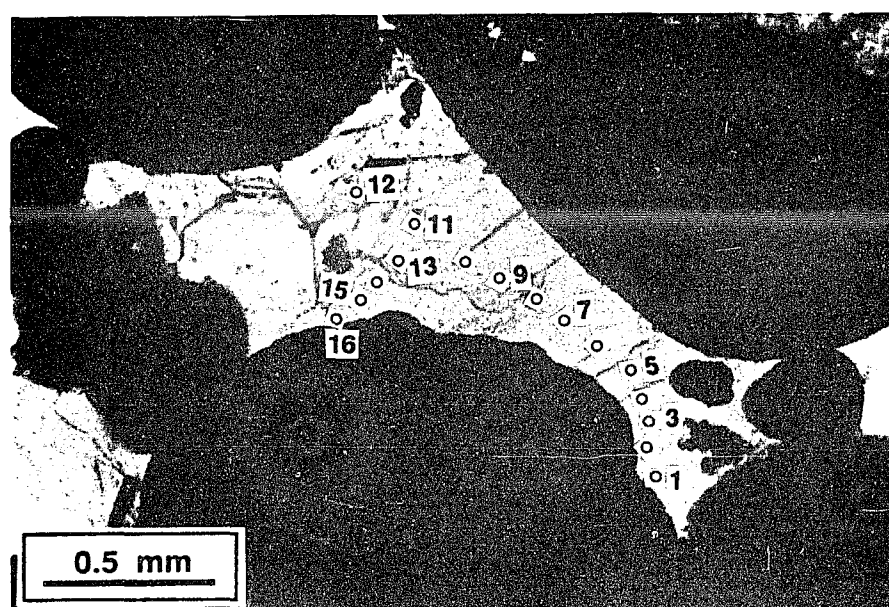
filled by zones 3-5 cements (Fig. 3.15).

The cited petrographic relationships between calcite zones and physical and chemical features indicate that cementation as early as zone 2 postdated pressure solution. The fact that most stylolite-related extension fractures are filled by zone 3-5 cements suggests that calcite released during pressure solution along stylolites were the source of these cement zones. The source of calcite that forms zone 2 cement however may have been initiated by grain-to-grain pressure solution and followed by stylolitization.

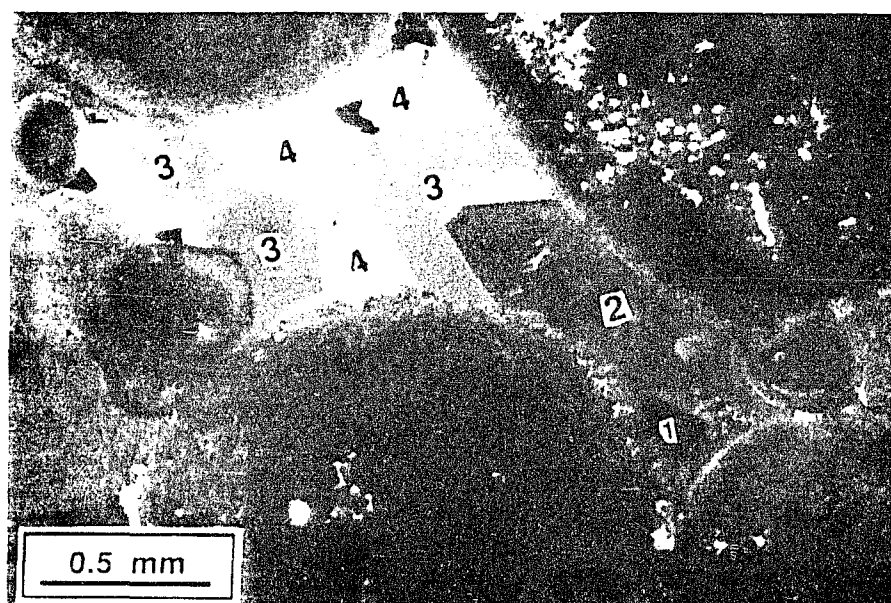
One bulk calcite sample has a $\delta^{18}\text{O}$ composition of -5.8 and a $\delta^{13}\text{C}$ composition of +3.5. Using the electron probe, a total of 16 points were analyzed for Mg, Sr, Fe, and Mn across the zoned cement shown in Figure 3.16. The results are presented in Table 3.4. The average Mg contents of zones 1-5 are 1629, 2153, 3365, 3989, and 3373 ppm, respectively. Their Mn values are <100, 144, 218, 1406, 939 ppm, respectively. Average Sr content of the points is about 100 ppm. The Fe content of all points is below detection limit of the instrument (<1pp). These data are in general agreement with those of Oglesby (1976).

The $\delta^{18}\text{O}$ compositions of three samples of calcite ooids range from -1.5 to -2.9 (average= -2.0) (Table 3.3). Their $\delta^{13}\text{C}$ compositions range from +3.9 to +4.4 with an average of +4.1. The ooids have an average concentration of 3619 ppm Mg, 310 ppm Sr, 32 ppm Fe, and 38 ppm Mn (Table 3.3).

Figure 3.16. (A) Plain light and (B) CL photomicrograph of zoned calcite cement showing first four zones and small part of zone 5. The solid circles in A are the locations of microprobe analyses. Shell #1 Evans 26-6, 3,920 m.



A



B

Table 3.4. Trace element composition (in ppm) of zoned calcite cement in Shell #1 Evans well. DL: below detection limit.

Point #	Mg	Mn	Zone #
1	2065	DL	1
2	1193	DL	1

3	2304	DL	2
4	1871	DL	2
5	2314	DL	2
6	1786	105	2
7	2315	DL	2
8	1771	205	2
9	2241	DL	2
10	2622	122	2

11	3351	215	3
12	3452	224	3
13	3292	215	3

14	3678	1424	4
15	4301	1388	4

16	3373	939	5

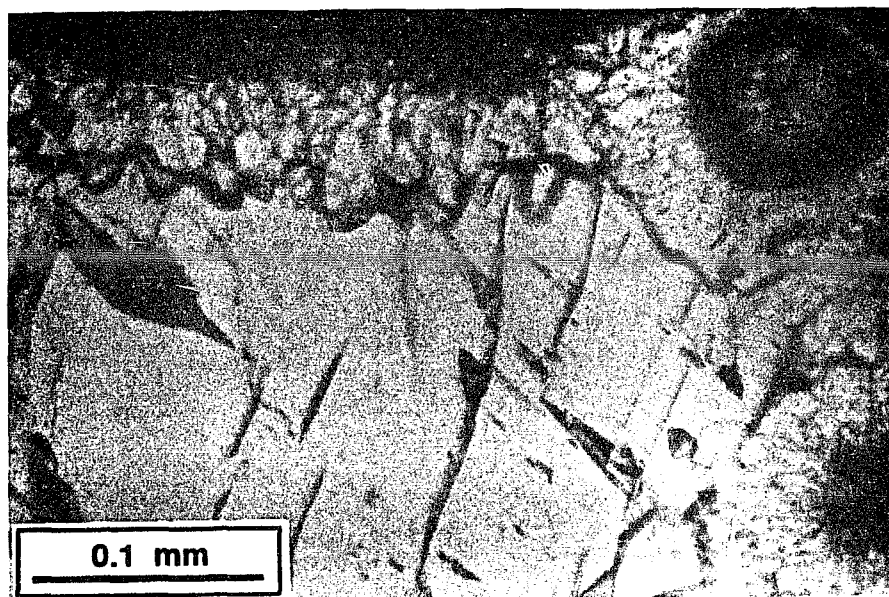
East Nancy Field

Three wells, Getty #1 Masonite 18-8, Getty #1 Allen 20-7, and Getty #1 Reddoch 15-10 (wells 7, 8, and 9, respectively, Figs. 3-6), were studied from this field. Calcite cements in all three wells exhibit four luminescent zones (Fig. 3.17). The luminescent intensities of zones 1 to 4 are non-luminescent (black), dull (brown), very bright (yellow), and moderately bright (orange). Zone 1 shows the commonly occurring irregular crystal interface with zone 2.

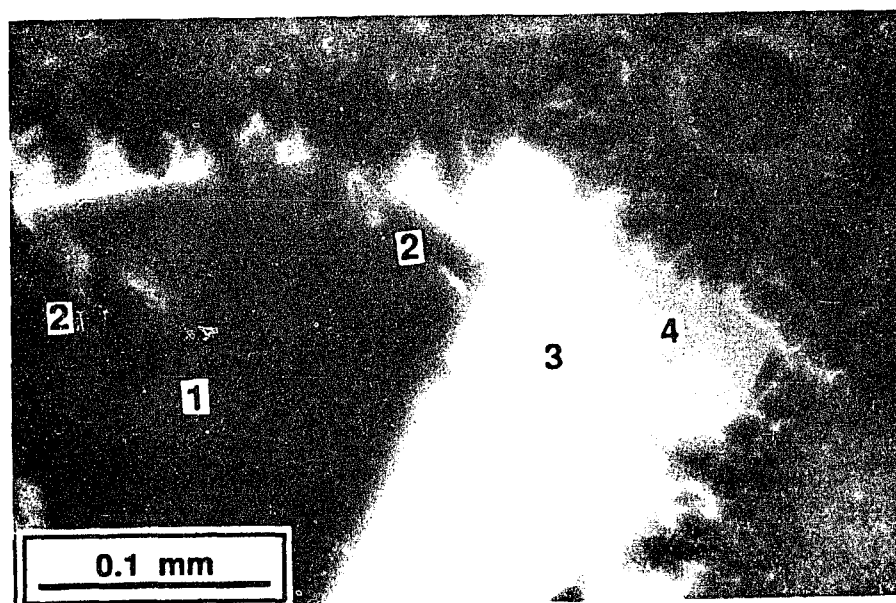
Petrographic and CL observations indicate that zone 1 cement postdates buckled ooids (Fig. 3.18). Zone 2 postdates grain fractures (Fig. 3.19), grain-to-grain pressure solution (Fig. 3.20), and is the oldest zone to fill stylolite related extension fractures (Fig. 3.21). These fractures, however, are dominantly filled by zones 3 and 4 (Fig. 3.21). It is therefore concluded that calcite cementation in this field is all post-pressure solution. Calcite released by grain-to-grain pressure solution precipitated as zone 2, and calcite generated by stylolitization precipitated as zones 3 and 4.

No probe analyses of these cements are available at this time. However, two samples composed primarily of zone 1 and 2 cement and two samples of zone 3 and 4 cement were analyzed with ICP for trace elements (Table 3.2). Zones 1-2 contain 2170 ppm Mg, 93 ppm Sr, <1 ppm Fe, and 30 ppm Mn. Zones 3-4 contain, 107 ppm Sr, 0 ppm Fe, and 325 ppm Mn. The

Figure 3.17. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing four zones in East Nancy field. Getty #1 Masonite 18-8, 4,133 m.

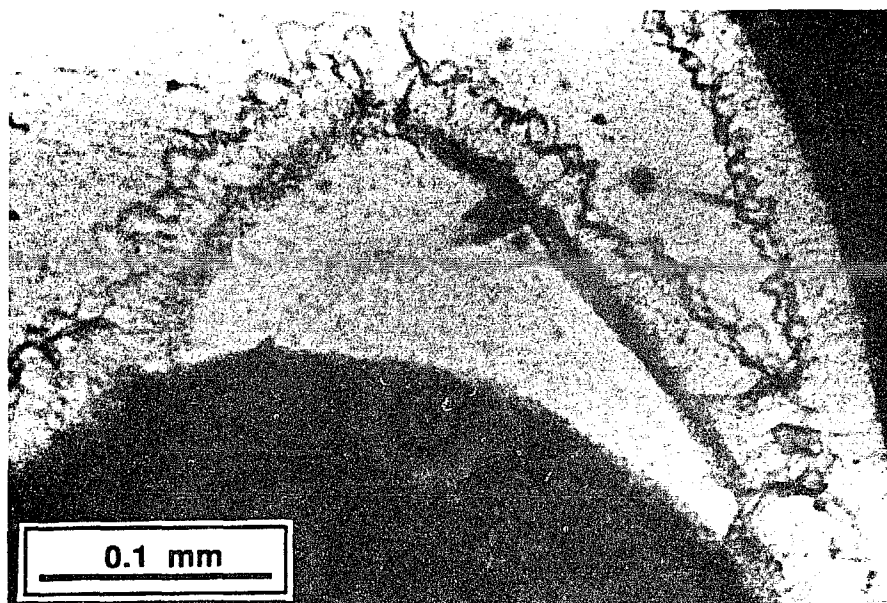


A

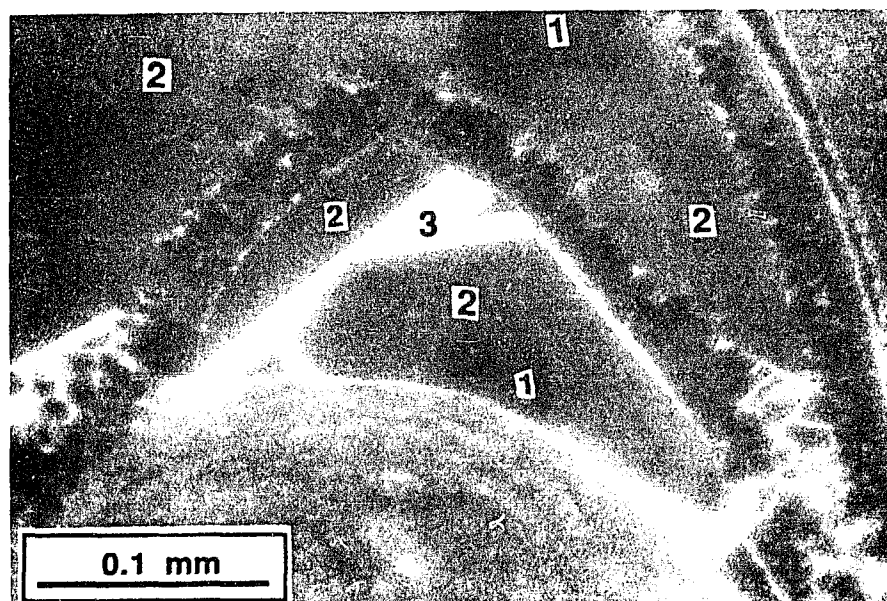


B

Figure 3.18. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing that zone 1 cement postdates ooid spalling. Getty #1 Masonite 18-8, 4,133 ft.

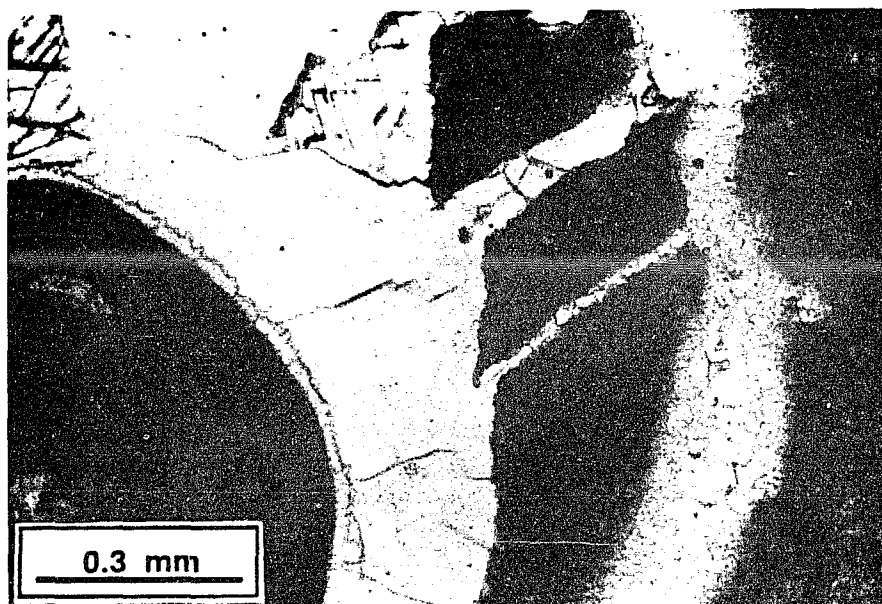


A

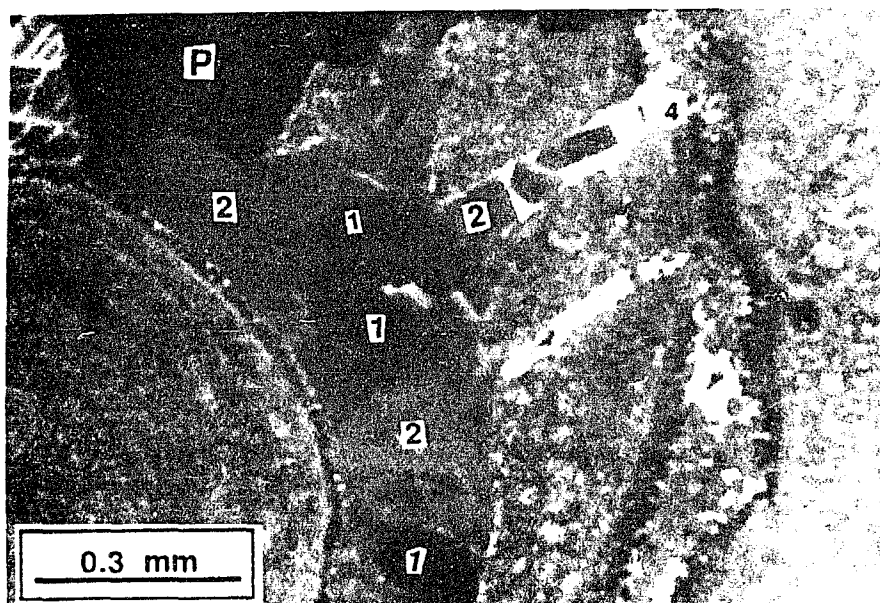


B

Figure 3.19. (A) Plain light and (B) CL photomicrographs showing that cementation as early as zone 2 postdates grain fracturing. Getty #1 Masonite 18-8, 4,133 m. P: Pore space.



A



B

Figure 3.20. (A) Plain light and (B) CL photomicrographs showing zone 2 calcite cement postdates grain-to-grain pressure solution. Getty #1 Masonite 18-8, 4,132 m.

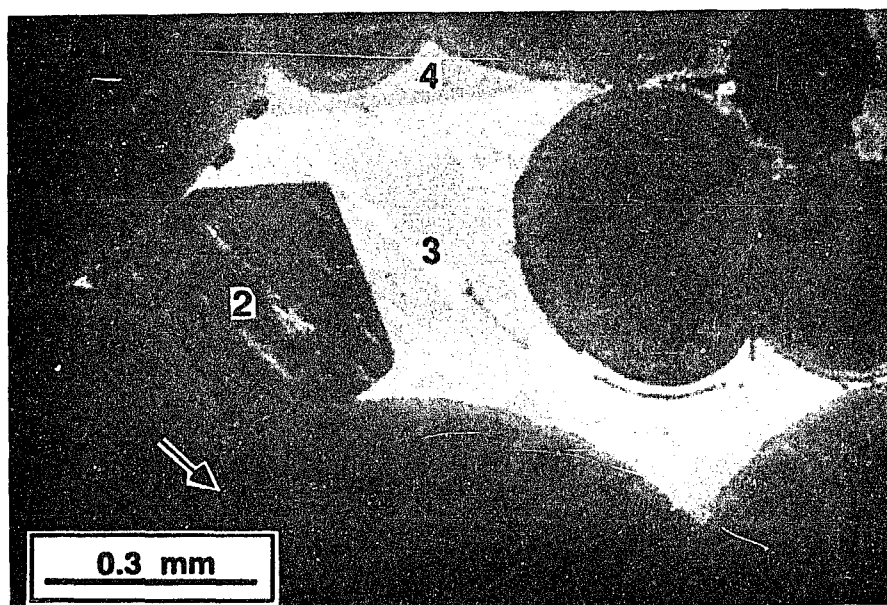
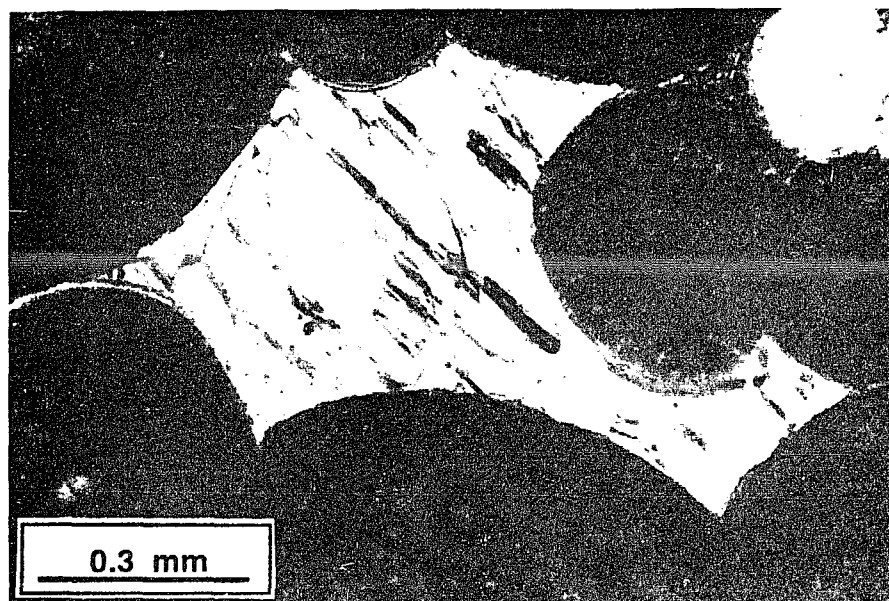
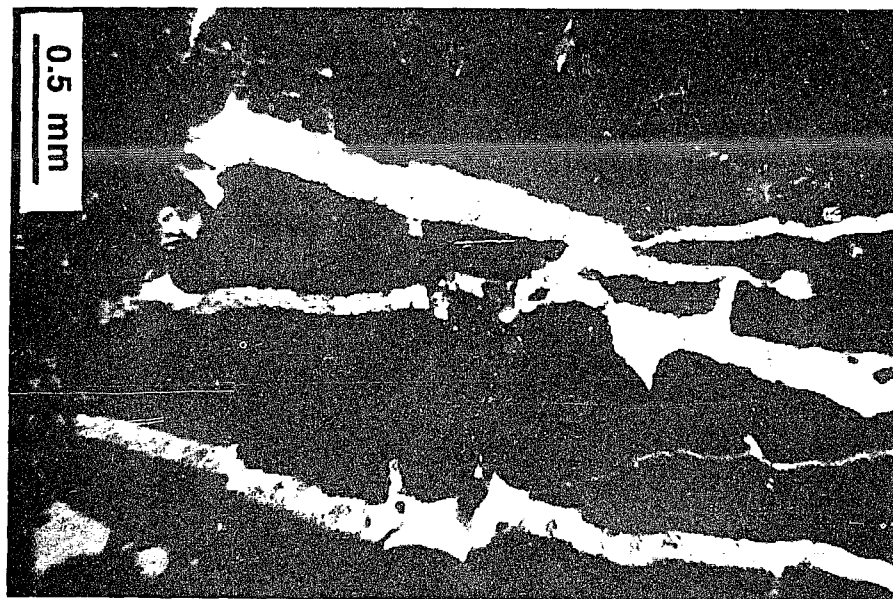
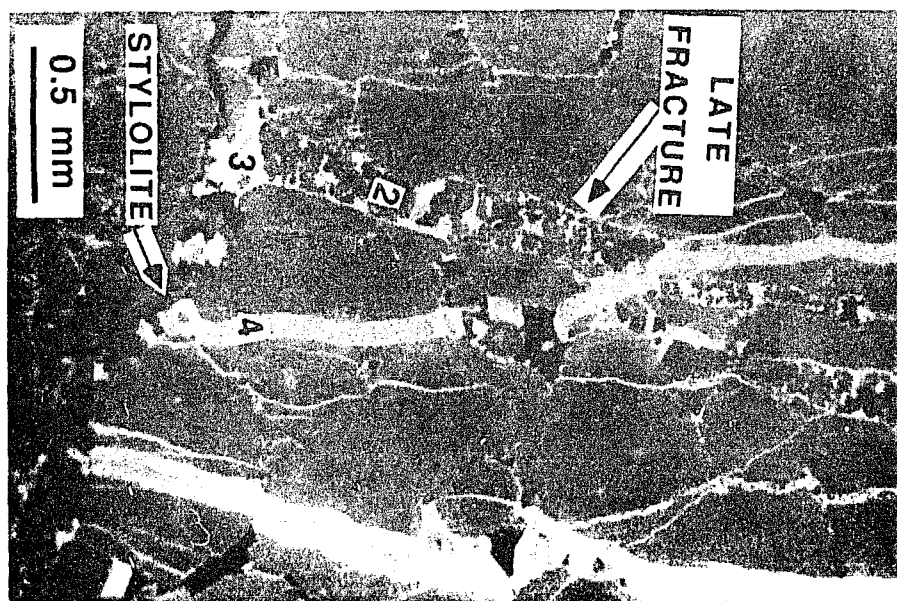


Figure 3.21. (A) Plain light and (B) CL photomicrographs of zoned cements filling late, stylolite-related, extension fractures. Small amounts of zone 2 cement are present in the fractures, indicating zone two slightly postdated stylolitization and rock fracturing. Getty #1 Reddoch 15-13, 4,169 m.



A



B

average $\delta^{18}\text{O}$ value of zones 1-2 is -5.6 and that of zones 3-4 is -8.2. The $\delta^{13}\text{C}$ composition of both samples is +4.6 (Table 3.2).

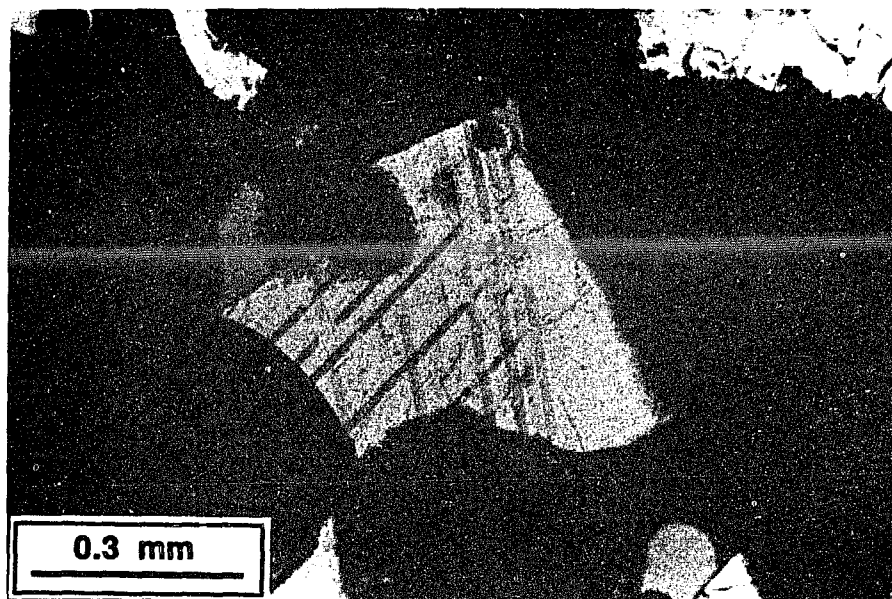
Four samples of originally calcitic ooids from the uppermost part of the Getty #1 Allen 20-7 well contain 3619 ppm Mg, 372 ppm Sr, 101 ppm Fe, and 36 ppm Mn (Table 3.3). Their $\delta^{18}\text{O}$ values range from -2.5 to -3.4 with an average of -2.9 and their $\delta^{13}\text{C}$ values range from +4.0 to +4.6 with an average of +4.2 (Table 3.3). In contrast to the Mosbacher #1 Board of Supervisors well, the $\delta^{18}\text{O}$ compositions of ooids become heavier from the top downward in the available core. All ooids show approximately the same the $\delta^{13}\text{C}$ composition (+4.2).

Goodwater Field

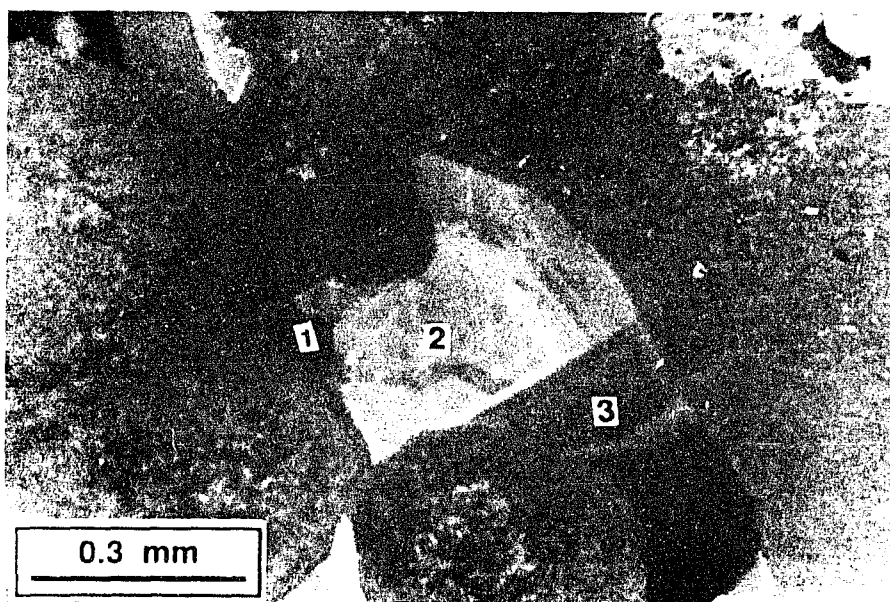
Shell #1 Ruter (well 10, Figs. 3-6) was studied from this field. Calcite cements in this well show three zones (Fig. 3.22). Unlike the cements in Pachuta Creek and East Nancy fields, all zones in the cements from this field are dull to non-luminescent. Zone 1 is non-luminescent (black), zone 2 is dull (light brown), and zone 3 is very dull (dark brown). Petrographic observations indicate that cementation as early as zone 1 postdates grain-to-grain pressure solution. Zones 2 and 3 fill stylolite-related extension fractures.

No probe analyses of individual zones from these

Figure 3.22. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing three zones. Getty #1 Ruter, 4,762 m.



A



B

cements are available at this time. However, three samples of bulk calcite cements, incorporating all three zones were analyzed for trace elements with ICP. They contain an average of 2665 ppm Mg, 104 ppm Sr, <1 ppm Fe, and 26 ppm Mn (Table 3.2). The average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the above samples are -5.5 and +4.1, respectively (Table 3.2).

Three samples of originally calcitic ooids from the upper most part of the well have 4079 ppm Mg, 253 ppm Sr, 00 ppm Fe, and 13 ppm Mn. The average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of ooids are -2.7 and +4.3, respectively (Table 3.3).

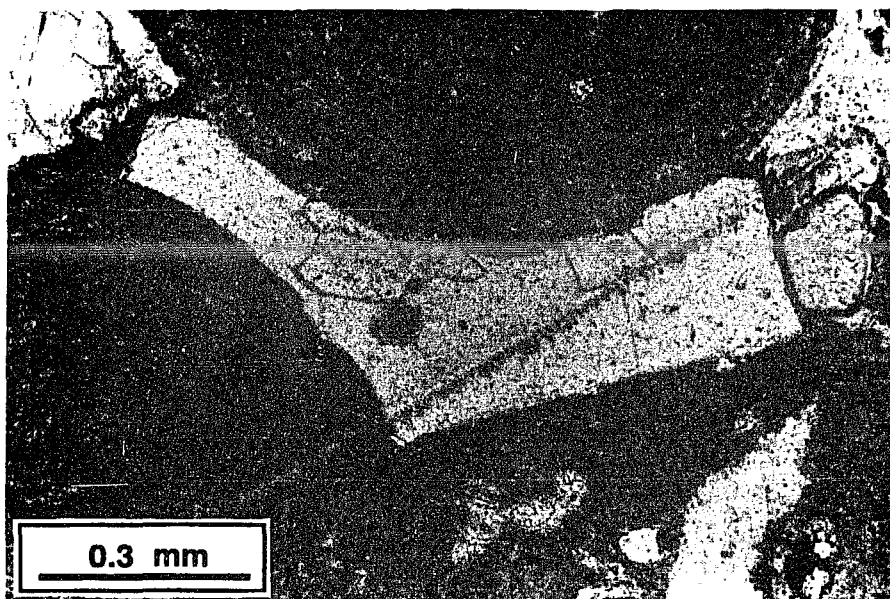
Garland Creek Field

Pruet & Hughes #1 Cooley 3-2 well (well 11, Figs. 3-6) was studied from this field. In contrast to the nearby Shell #1 Ruter well in Goodwater field where all cement zones were dull- to non-luminescent, cements in this well exhibit 5 distinct zones (Fig. 3.23). Zones 1 to 5 are: non-luminescent (black), dull (brown), bright (yellow), moderately bright (orange), and dull (brown). Petrographic observations indicate that zones 2-5 are post-pressure solution. No chemical analyses of cements and allochems are available from this field.

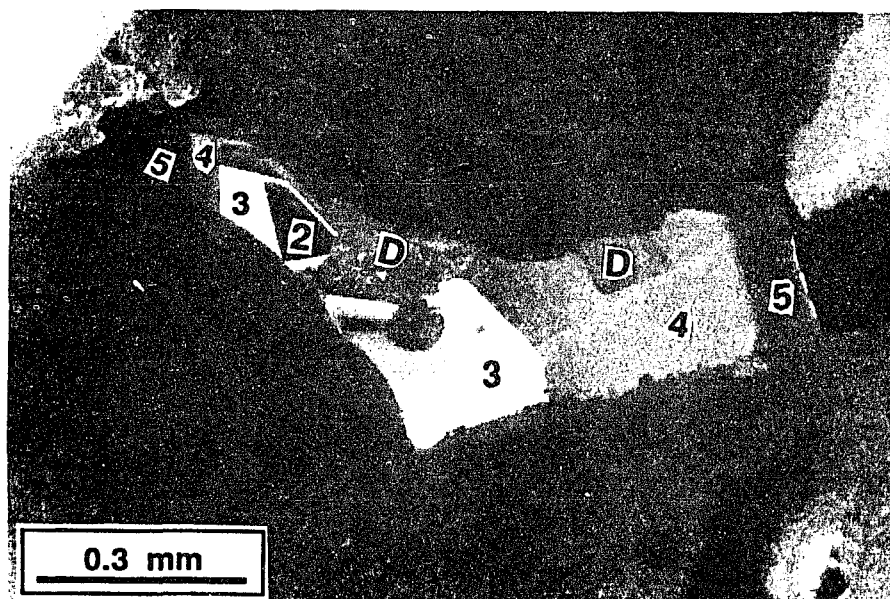
Saddle Dolomite and Late Anhydrite

Saddle dolomite exhibits luminescent zonation and occurs dominantly as pore-fill cement, and occasionally as a

Figure 3.23. (A) Plain light and (B) CL photomicrographs of zoned calcite cements showing five zones. Pruet & Hughes #1 Cooley 3-2, 4,748 m. D: Dolomite.



A



B

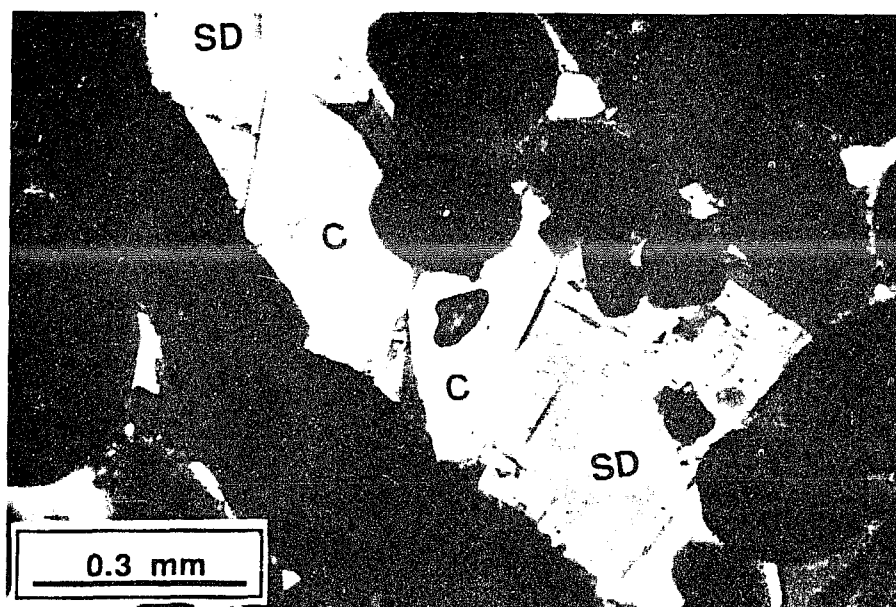
grain replacement. It occurs in all wells studied but is most common in East Nancy field. In this field, saddle dolomite postdates zone 4 calcite cement in some samples (Fig. 3.24), and it is postdated by zone 4 in others (Fig. 3.25). It is therefore concluded that saddle dolomite and calcite zone 4 probably precipitated close to the same time. Two samples of saddle dolomite from Sun #1 Board of Supervisors 16-13 have average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of -4.8 and +5.0, respectively (Table 3.2).

Late anhydrite occurs as a replacement as well as a cement. It consistently precipitated after saddle dolomite. It commonly exhibits euhedral crystals with orthorhombic terminations, indicating formation originally as anhydrite, rather than as pseudomorphs after gypsum.

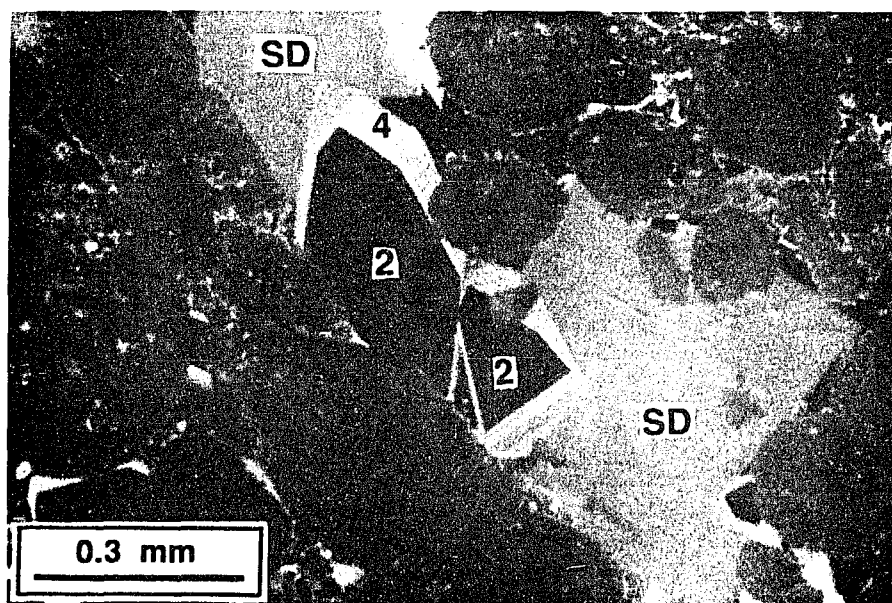
Solid Bitumen

Inorganic mineral cementation in Clarke County was apparently ended by the arrival of liquid hydrocarbons, probably due to poisoning of crystallization sites by hydrocarbons (Dunnington, 1967; Hancock and Scholle, 1975; Koepnick, 1985). The latest cement phase to precipitate is solid bitumen (organic cement) which clearly postdates calcite, saddle dolomite, and late anhydrite cements (Fig. 3.26). Precipitation of solid bitumen is the result of thermal destruction of liquid hydrocarbons (Rogers et al., 1974). Solid bitumen occurs as a major cement only in domain

Figure 3.24. (A) Plain light and (B) CL photomicrographs showing saddle dolomite (SD) which postdates zone 4 calcite cement. Getty #1 Masonite 18-8, 4,162 m.

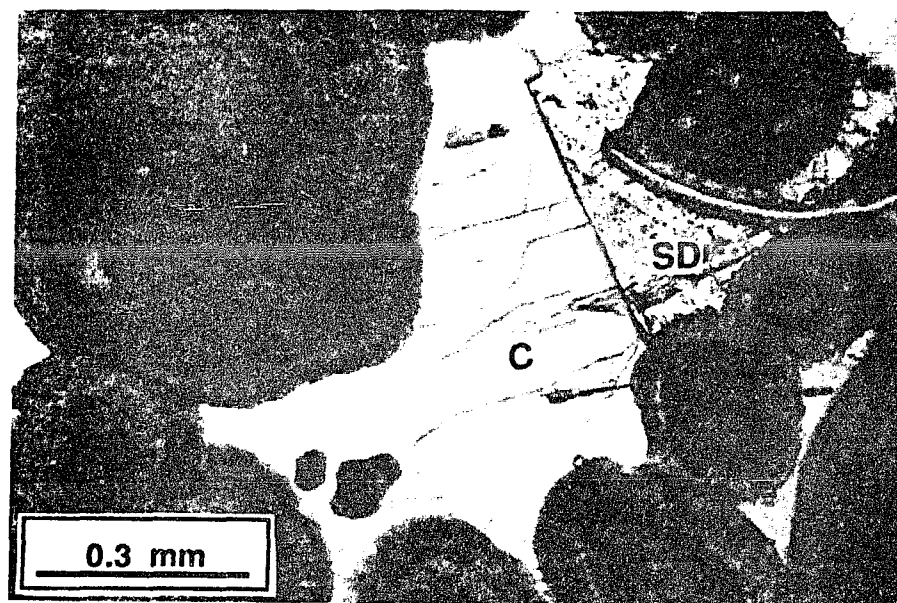


A

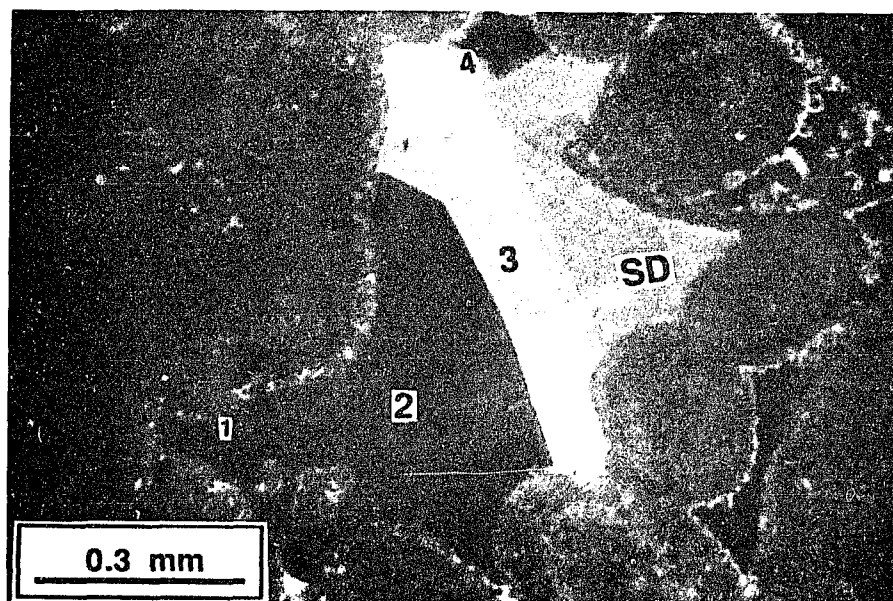


B

Figure 3.25. (A) Plain light and (B) CL photomicrographs showing zone 4 postdates saddle dolomite (SD). Getty #1 Masonite 18-8, 4,162 m.

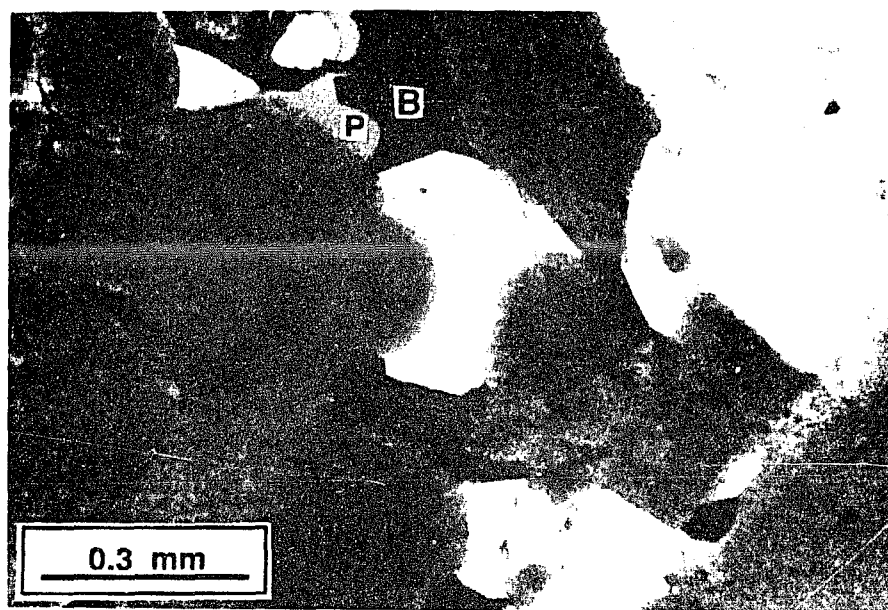


A

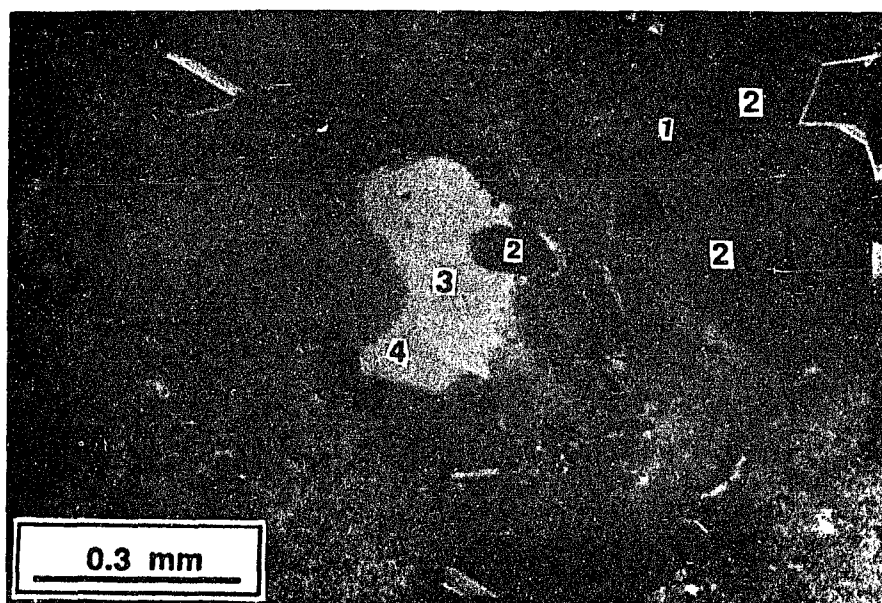


B

Figure 3.26. (A) Plain light and (B) CL photomicrographs showing that solid bitumen (B) postdates zone 4 cement. P: Pore space. Getty #1 Allen 20-7, 4,127 m.



A



B

4 and 5 (Fig. 3.3) where minimum reservoir temperatures are about 120 to 130 °C. It is therefore concluded that the main phase of solid bitumen precipitation is initiated near this temperature.

DEPTH OF CEMENTATION

Petrographic observations detailed above indicate that nearly all zoned calcite cements of the upper Smackover in Clarke County formed during burial and not early in a meteoric lens as was previously suggested (Oglesby, 1976). However, the exact time or depth of precipitation of each cement zone is not clear. Cementation in this area can not be correlated with events that can be constraints temporally (Meyers, 1974 1978; Kaufman et al., 1988). It is difficult to use oxygen isotopic values of the cements to estimate temperatures of formation because the $\delta^{18}\text{O}$ composition of the precipitational water is not known. The most conservative estimate that can be made is that cementation began after initiation of physical and chemical compaction and ceased with the arrival of liquid hydrocarbons. This restricts calcite cementation to a depth range of approximately 100 m to 3.5 km and a temperature range of 30 to 100 °C.

However, it was shown that cement zones can generally be correlated with physical and chemical compaction features such as grain-to-grain pressure solution, stylolites, and

rock fractures. Zone 2 calcite cement in Pachuta Creek, East Nancy, and Garland Creek fields and zone 1 of Goodwater field postdate grain-to-grain pressure solution but predate stylolites. Grain-to-grain pressure solution can begin at depths between 100 m to 1 km of burial depending on many factors including pore water chemistry, rate of burial, and sediment impurities (Schlanger and Douglas, 1974; Meyers, 1980; Meyers and Hill, 1983; Saller, 1985; James and Bone, 1989; Moore, 1989). Therefore, these burial cements could have begun to precipitate from 100 m to 1 km of burial at a temperature range of 30-60 °C.

Zones 3-4 of East Nancy field, 3-5 of Pachuta Creek, zones 2-3 of Goodwater field, and saddle dolomites apparently postdate stylolites. Stylolites and fractures associated with them are thought to be initiated at some 1-2 km of burial (Rutter, 1972; Anderson and Schneidermann, 1973; Alvarez et al., 1976; Buxton and Sibley, 1981; Meyers and Hill, 1983; Czerniakowski et al., 1984). Therefore, the calcite zones that postdate stylolites began to precipitate at a burial depth of at least 1 km. Cementation ceased when liquid hydrocarbons arrived in reservoirs, which according to thermal maturity calculations (Fig. 3.8), occurred at about 3.5 km of burial or near 100 °C. Therefore, these zones probably formed at a depth range of 1 to 3 km and a temperature range of 60 to 100 °C.

OXYGEN AND CARBON ISOTOPIC COMPOSITIONS OF BURIAL CEMENTS

The bulk calcite cements from Pachuta Creek, East Nancy, and Goodwater fields have $\delta^{18}\text{O}$ values ranging from -5 to -6, and a $\delta^{13}\text{C}$ value of about +4 (Table 3.2). However, analyses of individual or pair zones, especially in East Nancy field, indicate that younger cement zones become more depleted relative to ^{18}O (Fig. 3.27). The $\delta^{13}\text{C}$ values of all cements are close to each other and to that of the host rock (Table 3.2, Fig. 3.27). The variations of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ with depth seem to represent the burial trend of diagenetic phases precipitated before arrival of hydrocarbons and was previously recognized by Dickson and Coleman (1981), Moore (1985, 1989), Choquette and James (1987), and Zempolich et al. (1988). This trend suggests that the oxygen isotopic composition of the cements was continuously affected by temperature-dependent fractionation between water and carbonate minerals (O'Neil et al., 1969). Carbon isotopic values, on the other hand, were generally dominated by the composition of the host rock and were not significantly affected by temperature fractionation (Mook et al., 1974).

STRONTIUM ISOTOPIC COMPOSITION OF BURIAL CEMENTS

Sr isotopic values of samples from East Nancy field are shown in Figure 3.28. The average Sr isotopic value of calcite zones 1-2 is 0.70724 and that of zones 3-4 is 0.70840 (Table 3.2). Zones 3-4 from the Sun #1 Board of

Figure 3.27. Carbon and oxygen isotopic compositions of ooids, calcite cements, and saddle dolomite.

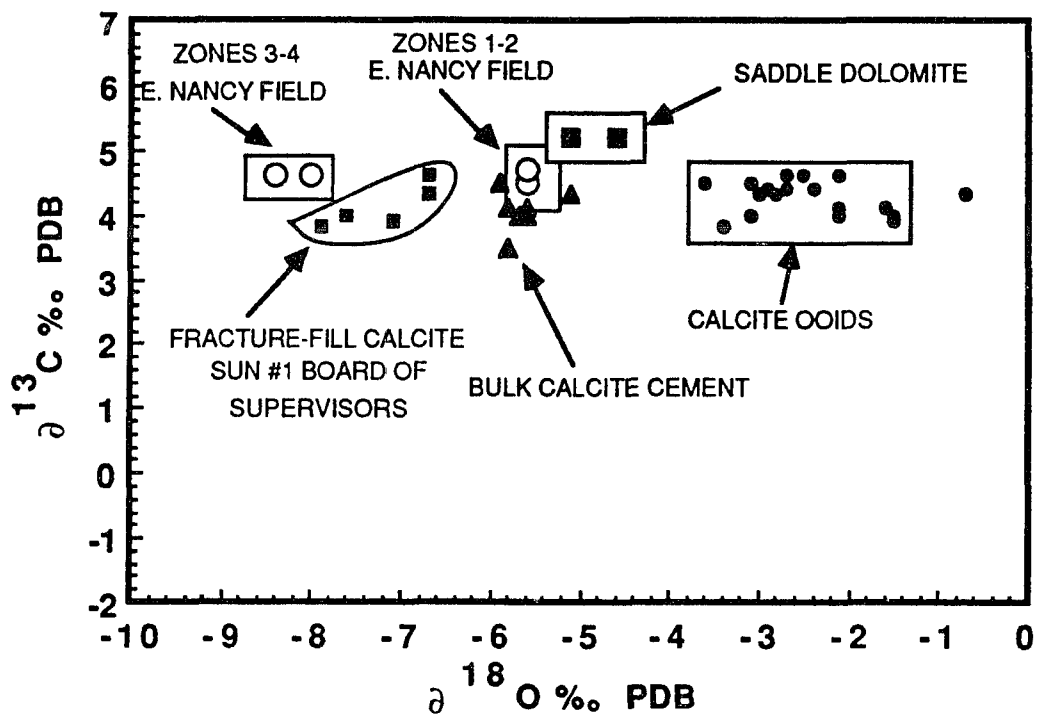
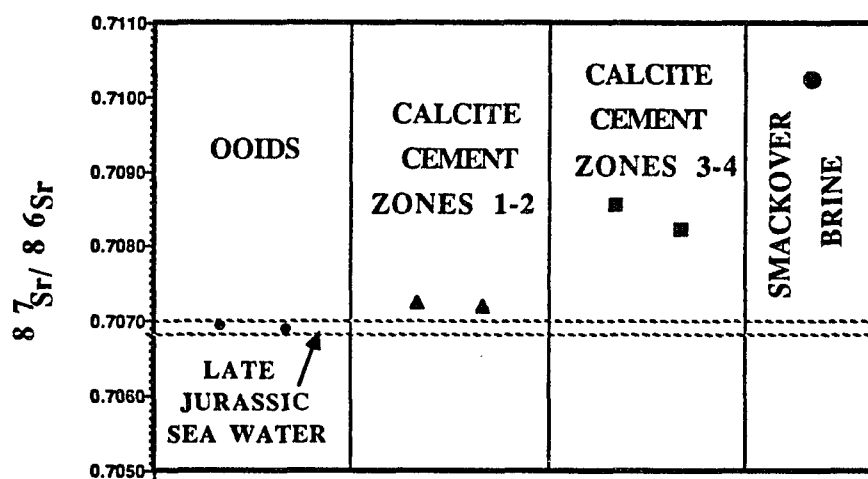


Figure 3.28. Strontium isotopic compositions of Late Jurassic sea water, zone 1-2 calcite cement, zone 3-4 calcite cement, and the present day Smackover brine from East Nancy Field. Strontium isotopic value of the brine from Russell (1985).



Supervisors 16-13 have an average Sr isotopic value of 0.70812. Two samples of ooids from East Nancy field have an average Sr isotopic value of 0.70693 (Table 3.3). The Sr isotopic composition of the present Smackover brine in East Nancy field is 0.71025 (Russell et al., 1989). Younger calcite cement zones exhibit a more radiogenic Sr isotopic composition than the older cement zones. This indicates that a significant volume of radiogenic Sr was imported into the system during precipitation of the younger cement zones (see also Moore, 1985, Woronick and Land, 1985).

TRACE ELEMENTS COMPOSITIONS OF BURIAL CEMENTS

The Mg contents of bulk cements range from 1327 to 3575 ppm. This suggests that diagenetic fluids had a very low Mg/Ca ratio. Low Mg concentration does not necessarily imply meteoric fluids because the Mg/Ca ratio of subsurface waters in the Mississippi salt basin is even lower than that of meteoric waters (Fig. 3.29). Therefore, low Mg values are consistent with the burial origin of the cements.

Of interest is an increase in Mg content from zone 1 to zone 4 and a decrease from zone 4 to zone 5 in the zoned calcite cement from Pachuta Creek field (Fig. 3.30). This trend was also found by Oglesby (1976). The reasons for the Mg trend are not clear. The distribution coefficient of Mg in calcite is less than one and increases with increasing temperature (Katz, 1973; Fuchtbauer and Hardie, 1976; Mucci

Figure 3.29. Molar Mg/Ca ratios of pore waters as a function of depth in the Mississippi salt basin. Data from Carpenter et al (1974), Kharaka et al (1987), and R. D. Snelling (Unpublished data).

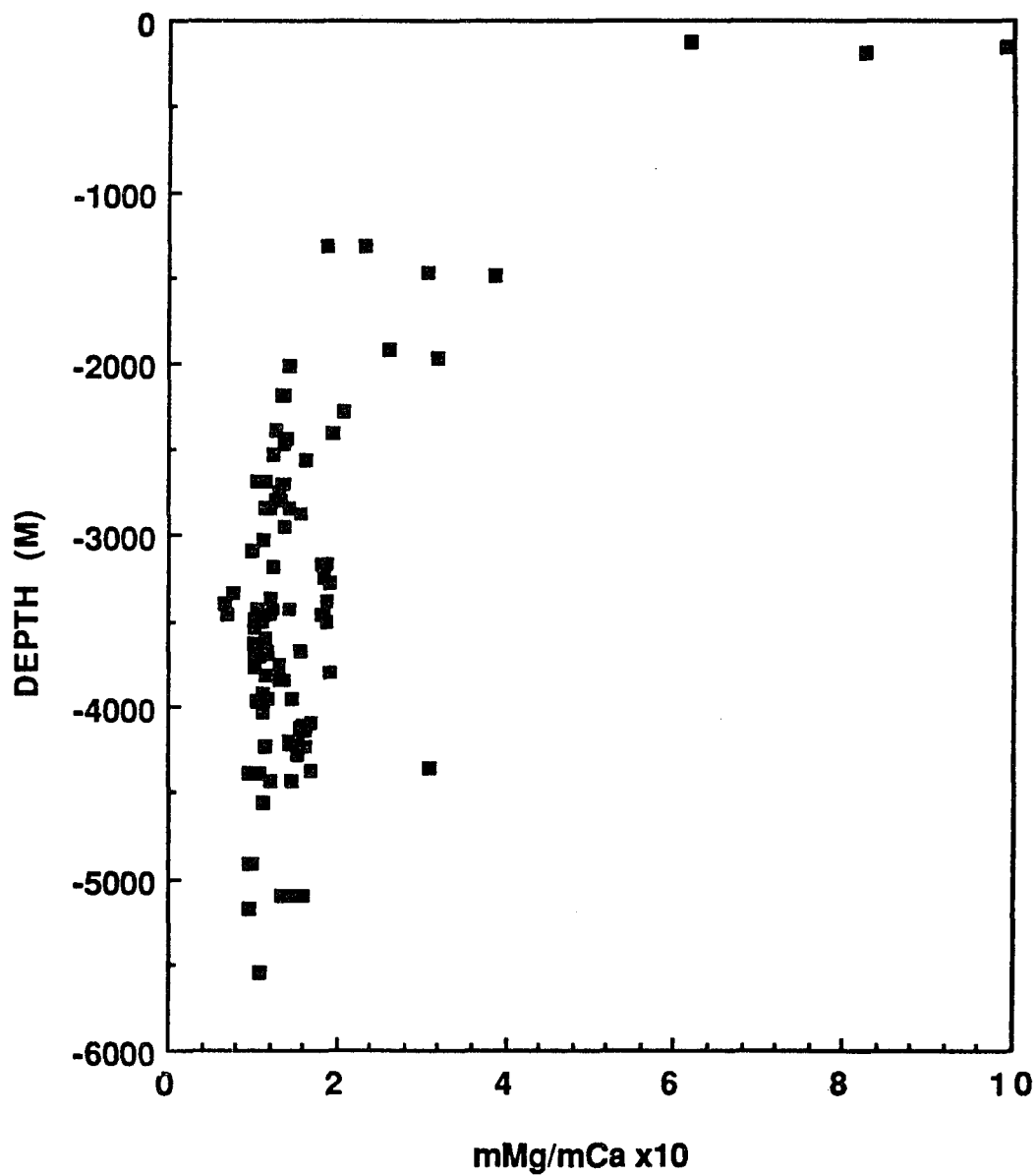
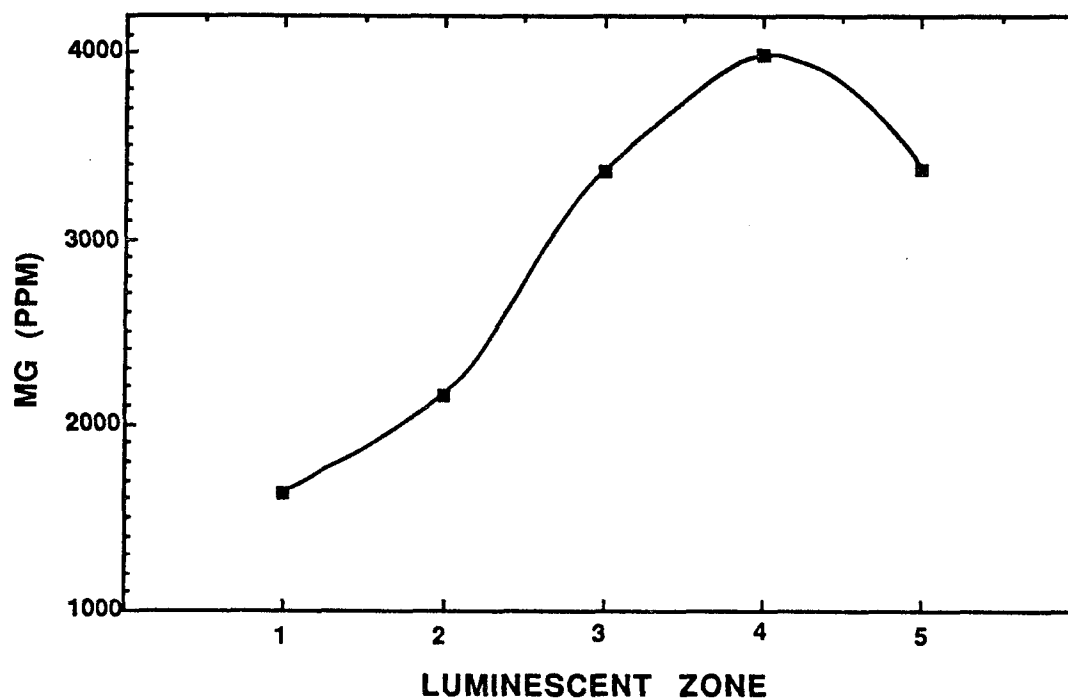


Figure 3.30. Average Mg contents of cement zones 1-5.
Locations of analysis points shown in Figure 3.16.



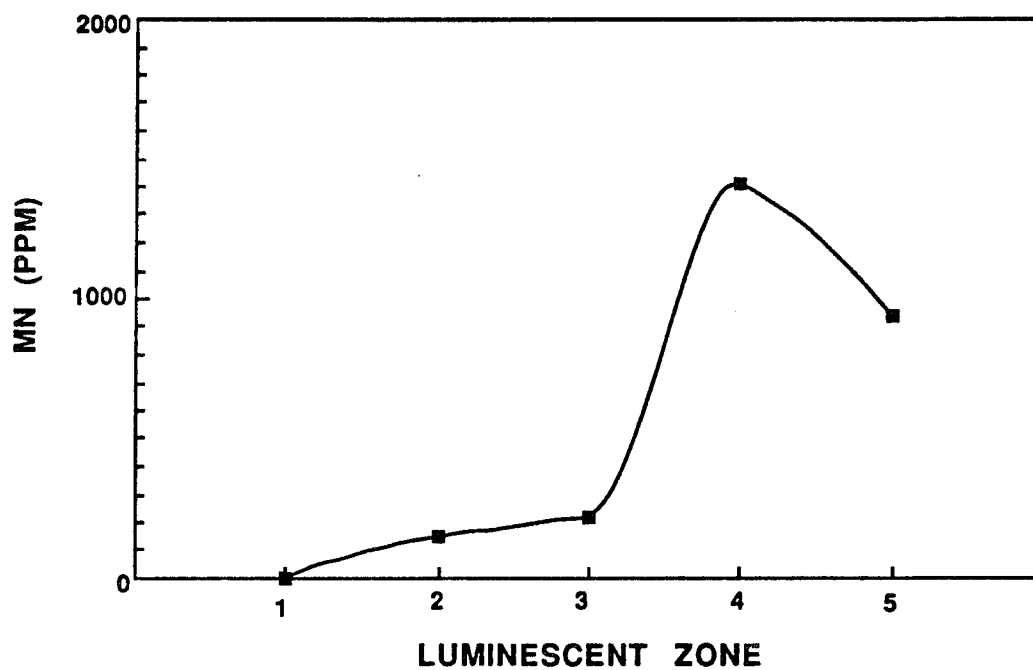
and Morse, 1983). In a relatively closed system, pore fluids become progressively enriched in Mg after precipitation of calcite. Therefore, successively precipitated calcite cements at nearly constant temperature should have progressively higher concentrations of Mg. Such a mechanism may explain the increase in Mg content across zones 1-4. Alternatively, the trend could result from precipitation of calcite from a pore fluid with constant Mg/Ca ratio at successively higher temperatures. The molar Mg/Ca ratio of pore waters in the Mississippi salt basin (Fig. 3.29) is about 1 near the surface (meteoric water), rapidly decreases to 0.1 at about 2 km, and remains relatively constant below this depth. If the Mg/Ca ratio of the Smackover pore water remained constant during burial, then the increase in Mg content of the cements may be interpreted as a result of the increase in the distribution coefficient with temperature. The Mg decrease from zone 4 to 5 suggests that Mg was removed from the pore waters. As was stated saddle dolomite coprecipitated with calcite cement very late in the paragenetic sequence. This may have lowered the Mg content of the pore waters, thereby decreasing Mg content in calcite zone 5.

The calcite cements show an average composition of 100 ppm Sr. In contrast to the Mg/Ca ratio, Sr/Ca ratio of subsurface fluids is significantly higher than meteoric water. However, it has been demonstrated that the

distribution coefficient of Sr decreases significantly as the rate of precipitation decreases and/or temperature increases (Kinsman, 1969; Lorens, 1980). Precipitation at an elevated temperature and a slow rate (typical of burial cements) has certainly affected the Sr incorporation in calcite (Moore and Druckman, 1981, Moore, 1985). However, it is also possible that the pore fluids that precipitated the calcite cements were not as strontium-rich as the present Smackover brine.

Mn contents of burial cements across the study area are highly variable. Calcite cements in the Sun #1 Board of Supervisors 16-13 have 400 to 900 ppm Mn. Calcite zones 1-2 in East Nancy field have 30 ppm Mn and calcite zones 3-4 from the same field exhibit about 300 ppm (Table 3.2). This certainly indicates variable Mn content of Smackover pore waters across Clarke County. Analyses of pore waters in the Mississippi salt basin (Carpenter et al., 1974; Kharaka et al., 1987) indicate that the Mn concentration of subsurface waters is highly variable. The Mn content of Smackover pore water in Clarke County, for example, ranges from <1 to 70 ppm (Carpenter et al., 1974; Kharaka et al., 1987). Mn content of calcite cement in Shell #1 Evans 26-6 increases from zone 1 to 4 and decreases from zone 4 to 5 (Fig. 3.31, Table 3.4) which indicate a direct correlation between Mn content and the luminescent intensity of the calcite cement. Incorporation of Mn in carbonates depends on Mn content of

Figure 3.31. Average Mn contents of calcite cement zones 1-5. Locations of analyses points shown in Figure 3.16.



pore water and on the redox potential of the diagenetic environment. The distribution coefficient of Mn, in contrast to Mg, is greater than 1 (Pingitore, 1978). Therefore, in a closed system, constant redox potential, and constant temperature, successive calcite zones should have lower Mn content. The molar Mn/Ca ratio in pore waters from the Mississippi salt basin show very scattered distribution with no apparent trends. This is probably due to differential input of Mn from various strata and differences in amount of H_2S present. The initial increase in Mn content may be a result of cementation in successively more reducing conditions. Alternatively, there may have been a steady import of Mn into the system. In addition, dissolution of the Smackover carbonates during stylolitization have contributed some Mn into the system.

Fe is present in significant amounts only in cements from the Sun #1 Board of Supervisors 16-13 well (well 3, Figs. 3-6). Fe content of pore waters in the Mississippi salt basin is highly variable (Carpenter et al., 1974; Kharaka et al., 1987). The Fe content of the Smackover brine, for example, ranges from 0 to 200 ppm. This variation in Fe concentration of burial fluids is the main reason for the variable Fe values in the cements. However, Fe contribution from the Smackover allochems during pressure solution is also an important factor.

BURIAL CEMENTATION HISTORY

Figure 3.32 summarizes the luminescent pattern of zoned calcite cements across Clarke County. Calcite growth in all calcite cements began with a non- to very dull luminescent zone and continued with a dull, a bright, and another dull zone (Fig. 3.32). Calcites, however, differ in luminescent intensity and number of zones. Any interpretation of burial cements must take into account the similarities and differences in calcite cement zonation as well as ^{18}O depletion and radiogenic Sr enrichment trends from older to younger cement zones.

It was shown that almost all zones of zoned calcite cements precipitated during burial and after compaction (Fig. 3.33B). Growth of zoned calcite cements began by precipitation of dull and non-luminescent cement zones (zones 1 or 1 and 2) when sediments were buried sufficiently deep (100 m to 1 km) for grain-to-grain pressure solution to begin. Very dull and non-luminescent intensities of these zones are result of either oxygenated environment or lack of Mn in the pore waters. However, it is possibly due to lack of Mn in a reduced environment. For example, non-luminescent zone 1 calcite cements from Goodwater field was precipitated after pressure solution. It is unlikely that the Smackover aquifer was oxygenated at the time of precipitation of this cement. Non luminescence of this zone is due to lack of Mn in pore waters in Goodwater field.

Figure 3.32. Patterns of zonation in calcite cements across
Clarke county.

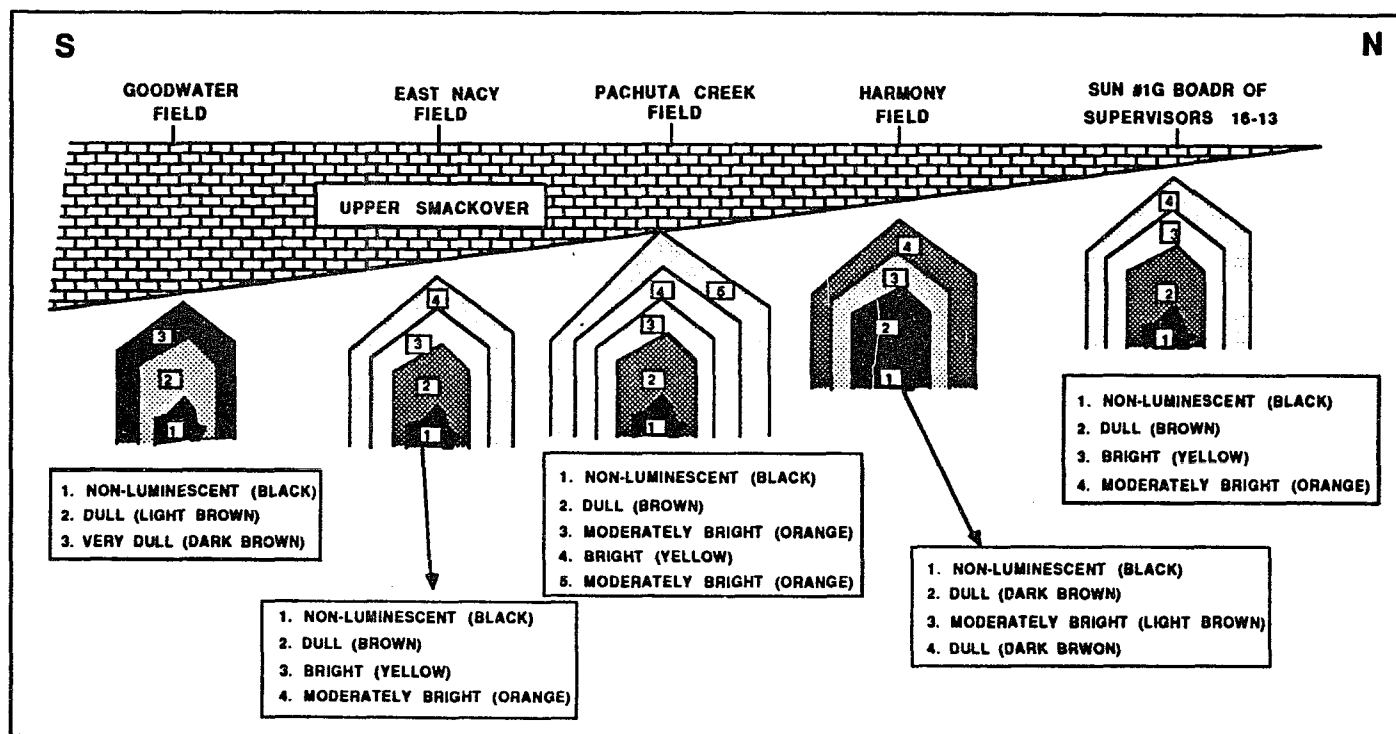
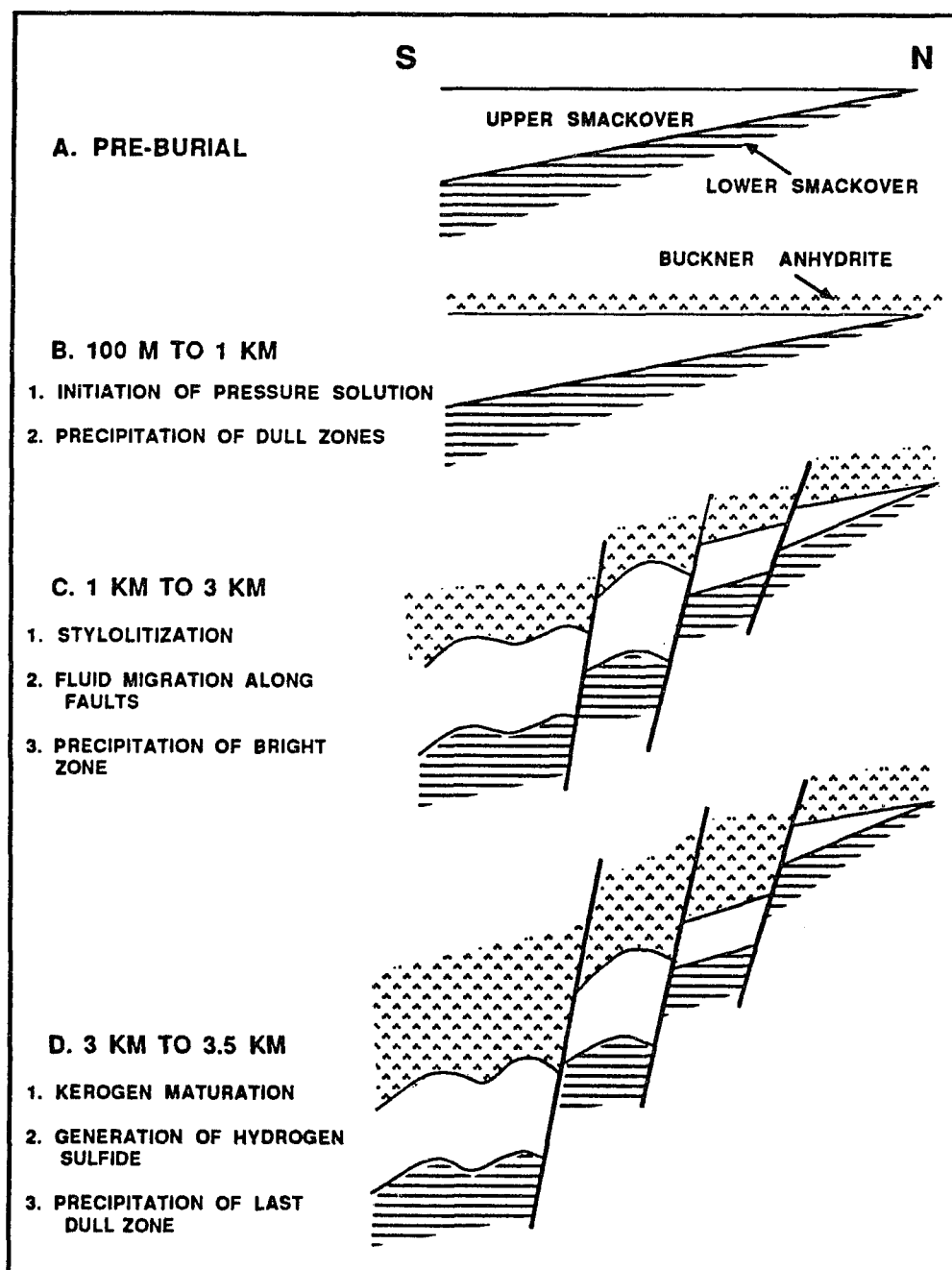


Figure 3.33. Simplified diagenetic and hydrologic model to explain sequential zonation and variations in oxygen isotopic composition and radiogenic Sr isotope chemistry of the upper Smackover calcite cements in Clarke County.



Mn and radiogenic Sr-rich brightly luminescent zones precipitate with further burial and after stylolitization. Mn and radiogenic Sr content of these zones were probably imported into the Smackover grainstones by fluid migration along faults which were activated by salt movement (Fig. 3.33C). Continued movement along faults and deeper burial may have produced isolated aquifers (Fig. 3.33D). Maturation of kerogen in source facies and generation of H_2S might have removed some of Fe and Mn from the pore fluids, resulting in dull luminescent intensity of the youngest dull cement zones. Hydrocarbon migration ended inorganic cementation. Thermal destruction of hydrocarbons in domain 4 and 5, which were exposed to temperatures high enough for thermal cracking of liquid hydrocarbons, resulted in precipitation of abundant solid bitumen.

CALCITE CEMENT STRATIGRAPHY

Calcite cement zones have been correlated for distances of over 100 km, used to infer chemical conditions of cementation environment, and related to occurrence of major geologic events (Meyers, 1974, 1978; Oglesby, 1976; Grover and Read, 1983; Dorobek, 1987; Hurley et al., 1988; Kaufman et al., 1988; Neimann and Read, 1988). In contrast, other studies have demonstrated that similar zones could not be recognized from pore to pore within a single sample (Searl, 1988).

The patterns of luminescent zonation in calcite cements from Clarke County differ from those previously reported (Meyers, 1974, 1978; Kaufman et al., 1988; Searl, 1988). The cements studied by these authors contain several alternations of non- and bright luminescent zones. This is generally thought to indicate influx of oxygenated meteoric water from a recharge area. This interpretation is supported by the presence of similar luminescent zonation in present day fresh water aquifers (James and Bone, 1989). In addition, successive influx of undersaturated meteoric water in some cases is recorded as corrosion of previously formed cement zones (Kaufman et al., 1988). The alternation of non-luminescent to bright luminescent cement zones are not seen in the calcite cements from Clarke County (Fig. 3.32). The difference between zonation seen in the calcite cements from Clarke County and zonation previously reported from Paleozoic carbonates is due to a major difference between the diagenetic system presented in this study and those reported from Paleozoic rocks. The Paleozoic sequences from which zoned cements are reported were generally exposed to long episodes of meteoric flushing (Meyers, 1974, 1978; Hurley et al., 1988; Kaufman et al., 1988; Neimann and Read, 1988; Searl, 1988). Although some meteoric diagenesis may have occurred during post-deposition and early burial of the Smackover Formation, such a system apparently did not continue and this formation became a confined aquifer soon

after burial. Lack of alternation of non- and bright luminescent zonation, absence of corrosion of any cement zone, and gradual variations in the intensities of luminescence of zones support this interpretation and suggest that the luminescent zonation seen here is characteristic of continuous cementation under progressive burial with no interruption.

OXYGEN ISOTOPIC EVOLUTION OF SMACKOVER PORE WATER

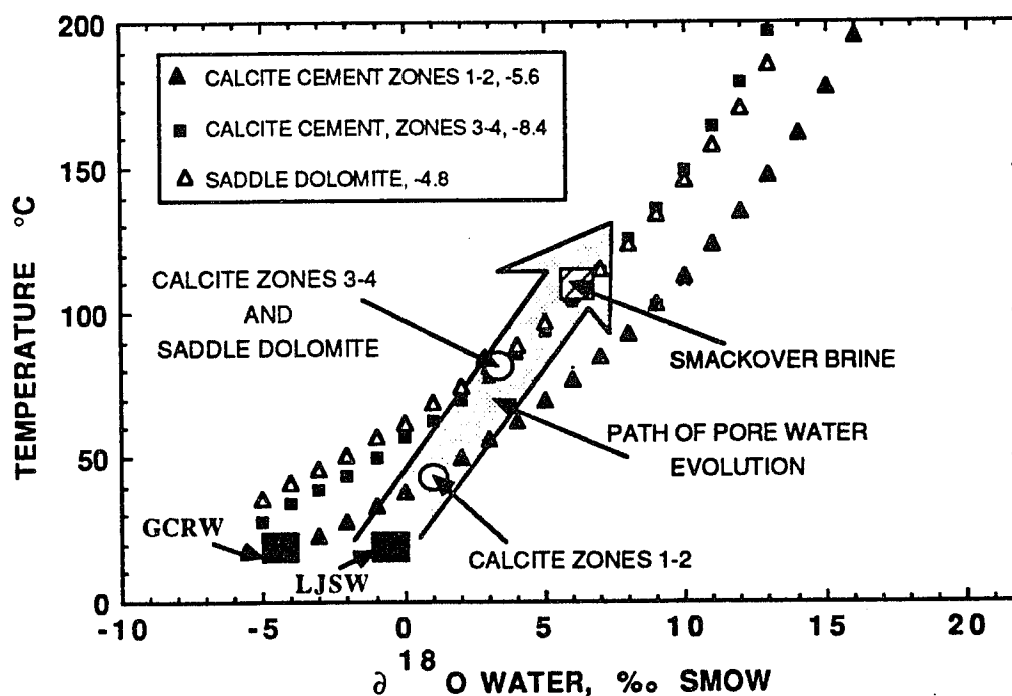
The present Smackover pore waters are thought to have formed by subaerial evaporation of sea water during deposition of the Louann Salt and then migrated into the Smackover Formation as a result of dewatering of the salt (Kharaka et al., 1987). Its present $\delta^{18}\text{O}$ composition (+6 SMOW, Kharaka et al., 1987) is also thought to be that of evaporated sea water during Louann time (Kharaka et al., 1987). This implies that the $\delta^{18}\text{O}$ value of the Smackover pore water did not change since it was formed in the Middle Jurassic. In addition, if the brine migrated into the Smackover Formation before the initiation of cementation, the above scenario also implies that all burial cements in the Smackover Formation have precipitated from a pore water with a $\delta^{18}\text{O}$ composition of +6. By the end of Smackover deposition the Louann Salt was buried over 600 m in the Mississippi salt basin. Casas and Lowenstein (1989) showed that halite loses over 95% of its pore waters during the

first 1 m of burial. Therefore, it is difficult to envision how Smackover pore water could have been generated from compaction of the Louann Salt after it had been buried for almost 1 km.

Oxygen and Sr isotopic compositions of calcite and dolomite cements in Clarke County are not in equilibrium with the oxygen and Sr isotopic composition of the present Smackover brine. The $\delta^{18}\text{O}$ composition of calcite cements ranges from -5 to -8.5, and the $\delta^{18}\text{O}$ composition of saddle dolomite is -4.8. Temperatures of 80, 110, and 105 °C, respectively, are required to precipitate these phases from a water with a $\delta^{18}\text{O}$ composition of +6. These temperatures are significantly higher than expected for the formation of the above phases. For example saddle dolomite samples are recovered from the Sun #1 Board of Supervisors where bottom hole temperature is 90 °C. This indicate that the pore water responsible for the calcite and dolomite cements in the Smackover Formation had a $\delta^{18}\text{O}$ composition lower than that of the present Smackover brine. Finally, and most importantly, the Sr isotopic compositions of calcite cements are significantly less radiogenic than the present Smackover brine (Fig. 3.28).

The oxygen isotopic compositions of the zoned calcite cements in East Nancy field have been used to reconstruct the oxygen isotope evolution of the Smackover pore water there (Fig. 3.34). Zones 1-2 have an average $\delta^{18}\text{O}$ value of

Figure 3.34. Oxygen isotopic evolution of the Smackover pore waters in Clarke County. Equation for calcite-water, $1000 \ln \alpha = 2.78 \times 10^6 \times T^{-2} - 3.39$ (O'Neil, et. al., 1969) and dolomite-water, $1000 \ln \alpha = 3.14 \times 10^6 \times T^{-2} - 2.0$ (Land, 1983). Oxygen isotopic composition of Late Jurassic sea water (LJSW) is derived from the oxygen isotope composition of Belemnite (Tan and Hudson, 1974, Fisher and Arthur, 1977). Oxygen isotopic composition of the Smackover brine from Kharaka et al. (1987) and that of Gulf Coast rain water (GCRW) from Sheppard (1986).



-5.6 and precipitated from near the surface to a depth of about 1 km. Assuming a surface temperature of 25 °C and geothermal gradient of 25 °C/km, it can be reasonably assumed that zones 1-2 precipitated at an average temperature of 40 °C. Zones 3-4 have an average $\delta^{18}\text{O}$ composition of -8.2. Zones 3-4 began to precipitate at an approximate depth of 1 km (50 °C) and their precipitation ended by the arrival of hydrocarbons (3 km, and 100 °C). Therefore, an average temperature of 70 °C is estimated for the precipitation of zones 3-4. Using the equation of O'Neil et al. (1969) it can be calculated that zones 1-2 precipitated from a water with a $\delta^{18}\text{O}$ composition of +1 ‰ SMOW followed by zones 3-4 and saddle dolomite from a water with a $\delta^{18}\text{O}$ value of +3 to +4 ‰ SMOW (Fig. 3.34). This pore water evolution suggests that the present +6 oxygen isotopic composition of the Smackover brine could have been derived by the continuous reaction of an original marine pore water with Smackover carbonates under progressively higher burial temperatures. Such continuous rock buffering is not unlikely. Kharaka and Carothers (1986) reported pore waters with $\delta^{18}\text{O}$ composition as high as +8 from the North Slope of Alaska which they thought was originally meteoric water of Tertiary age. In addition, $\delta^{18}\text{O}$ compositions of subsurface pore waters in the Mississippi salt basin vary linearly from -4 near the surface to +7 at 4.5 km regardless of lithologic boundaries (Kharaka et al., 1987). This linear variation is

similar to the general $\delta^{18}\text{O}$ trend of pore waters with depth in many sedimentary basins (Clayton et al., 1964; Sheppard, 1986). The linear trend does not indicate a change in the oxygen isotopic composition of sea water through time. It may suggest a mixing of a heavy oxygen source at depth, and a light oxygen reservoir at the surface. The input of heavy oxygen is most likely due to rock-water interaction involving Smackover carbonates and mixing with light oxygen derived from meteoric water.

The Sr isotopic composition of the present Smackover brine in East Nancy field (0.71025, Russell, 1985) is more radiogenic than Late Jurassic sea water (0.7070, Burke et al., 1982). This suggests that significant amounts of radiogenic Sr have been imported into Smackover pore waters.

CONCLUSIONS

(1) The upper Smackover Formation can be divided into four domains with respect to lithology, grain mineralogy, early diagenesis (including dolomitization), and burial diagenesis. The most important characteristics of each domain are: originally aragonitic grains and early dolomitization in domain 1; originally aragonitic grains, early dolomitization and dissolution in domain 2; originally aragonite and calcite grains with moderate early and late diagenetic overprint in domain 3; originally calcite grains suffering intense burial diagenesis with little or no early

diagenetic overprint in domain 4.

(2) Marine diagenesis includes precipitation of circumgranular fibrous and bladed calcite cement and minor micrite cement. Early diagenesis includes dolomitization, dissolution of aragonitic grains, and precipitation of circumgranular bladed cement and equant calcite cementation.

(3) Burial events are zoned calcite cement, saddle dolomite, and anhydrite.

(4) The zoned calcite cements show a similar sequence of zonation across the area starting with a non-luminescent zone followed successively by a dull, a bright, and another dull zone. The intensity of luminescence and the number of zones vary across the study area.

(5) Petrographic observations indicate that in contrast to previous interpretations, the zoned calcite cements in the study area did not precipitate early in a meteoric lens, but formed late at burial depths of 100 m to 3.5 km and at temperatures ranging from 30 to 100 °C.

(6) All zoned calcite cements show similar Sr content (about 100 ppm) and variable Fe and Mn (0 to 1000 ppm). The Mg content of bulk zoned calcite cements range from 1327 to 3557 ppm. Mg and Mn values of calcite cement zones in Pachuta Creek field increase from zone 1 to 4 and decrease from 4 to 5. The Mg trend is thought to be the result of precipitation from a fluid with constant Mg/Ca ratio at successively higher temperatures during burial. The final

decrease in Mg is due to simultaneous precipitation of saddle dolomite which reduced Mg/Ca ratio of pore fluids. The increase in Mn is thought to represent precipitation under progressively more reducing conditions combined with import of Mn into the system.

(7) Older cement zones have a high $\delta^{18}\text{O}$ value (about -5) and a non-radiogenic Sr signature (0.7070). Younger cement zones have a lower $\delta^{18}\text{O}$ value (about -8) and a more radiogenic Sr content (0.7081). This supports an interpretation of precipitation under progressively higher temperatures with import of radiogenic Sr into the system.

(8) Oxygen isotopic compositions of calcite cements in East Nancy field indicate that Smackover pore waters had the isotopic composition of Late Jurassic sea water and became progressively heavier by continuous interaction with Smackover carbonates.

ACKNOWLEDGEMENTS

Thanks to my dissertation advisor Dr. C. H. Moore for his patience and constant constructive criticism of this research; To Shell, Sun, and Texaco petroleum companies for providing core materials. to T. Egler and the staff at Shell core warehouse for their generous help; to G. Herman, E. Stout, D. Stout, W. Dawson for core and petrophysical data; to L. S. Land for strontium isotope analyses and beneficial discussion. To R. Sassen, T. Dickson, J. S. Hanor, and J. L.

Banner for discussion and comments; to J. T. Eldridge and F. C. Meendsen for their help in environmental interpretation and core description. to R. D. Snelling for trace element analyses and beneficial discussion; to W. LeBlanc for x-ray diffraction analyses, S. Reed for providing technical assistance in the lab, K. Lyle for photography, and S. O. Moshier, I. P. Gill, and E. Tye for providing humor; to B. Delaville, M. Moore, F. Couvillon, and C. Weber for keeping us all happy and their logistical support; to all industrial associates members of the Applied Carbonate Research Program for constructive comments at the annual meetings; and very special thanks to M. L. Machain for her support and assistance during the course of this study. B. L. Kirkland and W. J. Wade reviewed the manuscript and offered constructive comments. This research was supported by the Department of Geology, Applied Carbonate Research Program, and Basin Research Institute of the Louisiana State University.

REFERENCES CITED

- Alvarez, W., Engelder, T., and Lowrie, W., 1976, Formation of spaced cleavage and folds in brittle limestone by dissolution: *Geology*, v. 4, p. 698-701.
- Anderson, T. F., and Schneidermann, N., 1973, Stable isotope relationships in pelagic limestones from the central Caribbean: Leg. 15, Deep Sea Drilling Project: Initial Reports, Deep Sea Drilling Project, Washington, U.S. Government Printing Office, v. 15, p. 795-803.
- Assereto, R., and Folk, R. F. 1976, Brick-like texture and radial rays in Triassic pisolites of Lombardy, Italy: A clue to distinguish ancient aragonite pisolites: *Sedimentary Geology*, v. 16, p. 205-222.
- Badon, C. L., 1974, Petrology and reservoir potential of the upper member of the Smackover Formation, Clarke County, Mississippi: *Gulf Coast Association of Geological Societies Transactions*, v. 24, p. 163-174.
- Baria, I. R., Stout, D. L., Harris, P. M., and Crevello, P. D., 1982, Upper Jurassic reefs of the Smackover Formation: *American Association of Petroleum Geologists Bulletin*, v. 66, p. 1449-1482
- Becher, J. W., and Moore, C. H., 1976, The Walker Creek field: a Smackover diagenetic trap: *Gulf Coast Association of Geological Societies Transactions*, v. 26, p. 34-56.
- Brock, F. C., and Moore, C. H., 1981, Walker Creek

- revisited: A reinterpretation of the diagenesis of the Smackover Formation of Walker Creek Field, Arkansas: Gulf Coast Association of Geologic Societies Transactions, v. 31, p. 49-58.
- Buffler, R. T., and Sawyer, D. S., 1985, Distribution of crust and early history, Gulf of Mexico basin: Gulf Coast Association of Geological Societies Transactions, v. 35, p. 333-344.
- Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of sea water $87\text{Sr}/86\text{Sr}$ throughout Phanerozoic time: Geology, v. 10, p. 516-519.
- Buxton, T. M., and Sibley, D. F., 1981, Pressure solution features in a shallow buried limestone: Journal of Sedimentary Petrology, v. 51, p. 19-26.
- Carpenter, A. B., Trout, M. L., and Pickett, E. E., 1974, Preliminary report on the origin and chemical evolution of lead and zinc brines in central Mississippi: Economic Geology, v. 69, p. 1191-1206.
- Carpenter, S. J., Erickson, J. M., Lohmann, K. C, and Owen, M. R., 1988, Diagenesis of fossiliferous concretions from the Upper Cretaceous Fox Hills Formation, North Dakota: Journal of Sedimentary Petrology, v. 58, p. 706-723.
- Casas, E., and Lowenstein, T. K., 1989, Diagenesis of saline pan halite: Comparison of petrographic features of

- modern, Quaternary and Permian halites: *Journal of Sedimentary Petrology*, v. 59, 724-739.
- Choquette, P. W., and James, N. P., 1987, Diagenesis #12. Diagenesis in limestones - 3. The deep burial environment: *Geoscience Canada*, v. 14, p. 3-35.
- Clayton, R. N., Friedman, I., Graf, D. L., Meyeda, T. K., Meents, w. F., and Shimp, N. F., 1966, The origin of saline formation waters: *Journal of Geophysical Research*, v. 71, p. 3869-3882.
- Crevello, P. D., and Harris, P. M., 1985, Depositional models for Jurassic reefal buildups, in Ventress, W. P. S., Bebout, D. G., Perkins, R. F., and Moore C. H., eds, *The Jurassic of the Gulf Rim: Proceedings of third annual research conference of SEPM*, Baton Rouge, Louisiana, p. 57-102.
- Czerniakowski, L. A., Lohmann, K C., and Wilson, J. L., 1984, Closed-system marine burial diagenesis: Isotopic data from the Austin Chalk and its components: *Sedimentology*, v. 31, p. 863-877.
- Dickens, T. H., 1968, Jurassic stratigraphy of central and southern Mississippi: *Mississippi Geological Survey Bulletin*, v. 109, p. 9-37.
- Dickson, J. A. D., 1966, Carbonate identification and genesis as revealed by staining: *Journal of Sedimentary Petrology*, v. 36, p. 491-505.
- , and Coleman, M. L., 1980, Changes in

- carbon and oxygen isotope composition during limestone diagenesis: *Sedimentology*, v. 27, p. 107-118.
- Dorobek, S. L., 1987, Petrology, geochemistry, and origin of burial diagenetic facies, Siluro-Devonian Helderberg Group (carbonate rocks), central Appalachians: *American Association of Petroleum Geologists Bulletin*, v. 71, p. 492-514.
- Dunnington, H. V., 1967, Aspects of diagenesis and shape change in stylolitic limestone reservoirs: 7th World Petroleum Congress Proceedings, v. 20, p. 339-352.
- Eldridge, J. T., Upper Jurassic stratigraphy, porosity distribution, and hydrocarbon potential of western southern Mississippi: M. S. Thesis, Louisiana State University, 179p.
- Fisher, A. G., and Arthur, M. A., 1977, Secular variation in the pelagic realm, in Cook, H. and Enos, P., eds., Deep-water carbonate environments: SEPM, Special Paper 25, p. 19-50.
- Fletcher, R. C., And Pollard, D. D., 1981, Anticrack model for pressure solution surfaces: *Geology*, v. 9, p. 419-424.
- Fuchtbauer, H., and Hardie, L. A., 1976, Experimentally determined homogeneous distribution coefficients for precipitated magnesian calcites: *Geological Society of America, Abstracts of Annual Programs*, v. 8, p. 877.
- Grover, G., and Read, J. F., 1983, Paleoaquifer and deep

- burial related cements defined by regional cathodoluminescent patterns, Middle Ordovician carbonates, Virginia: American Association of Petroleum Geologists Bulletin, v. 67, p. 1275-1303.
- Hancock, J. M., and Scholle, P. A., 1975, Chalk of the North Sea, in Woodland, A. W. ed., Petroleum and the Continental Shelf of North-West Europe, v. 1: Wiley and Son, p. 413-425.
- Hughes, D. J., 1968, Salt tectonics as related to several Smackover fields along the northeast rim of the Gulf of Mexico basin: Gulf Coast Associations of Geological Societies transactions, v. 18, p. 320-330.
- Hurley, N. H., and Lohmann, K. C, 1989, Diagenesis of Devonian reefal carbonates in the Oscar Range, Canning Basin, Australia: Journal of Sedimentary Petrology, v. 59, p. 127-146.
- Imlay, R. W., 1980, Jurassic Paleobiography of the conterminous United State in its continental setting: USGS Professional Paper 1062, 134 pp.
- James, N. P., and Bone, Y., 1989, Petrogenesis of Cenozoic temperate water carbonates, south Australia: A model for meteoric/shallow-burial diagenesis of shallow water calcite sediments: Journal of Sedimentary Petrology, v. 59, p. 191-203.
- Katz, A., 1973, The interaction of magnesium with calcite during crystal growth at 25-90°C and one atmosphere:

- Geochemica et Cosmochemica Acta, v. 37, p. 1563-1586.
- Kaufman, J., Cander, H. S., and Daniels, L. D., and Meyers, W. J., 1988, Calcite cement stratigraphy and cementation history of the Burlington-Keokuk Formation (Mississippian), Illinois and Missouri: Journal of Sedimentary Petrology, v. 58, p. 312-326.
- Kharaka, Y. K., and Carothers, W. W., 1986, Oxygen and hydrogen isotope geochemistry of deep basin brines in Fritz, P., and Fontes, J. Ch., eds, Handbook of environmental isotope geochemistry, v. 2 the terrestrial Environment, B:... p. 305-360
- , Maest, A. S., Carothers, W. W., Law, L. M., Lamothe, P. J., And Fries, T. L., 1987, Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A., Applied Geochemistry, v. 2, p. 543-561.
- Kinsman, D. J. J., 1969, Interpretation of Sr^{+2} concentrations in carbonate minerals and rocks: Journal of Sedimentary Petrology, v. 39, p. 486-508.
- Koepnick, R. B., 1985, Distribution and permeability of stylolite-bearing horizons within a Lower Cretaceous carbonate reservoir in the Middle East: Society of Petroleum Engineers 14173, p. 1-5.
- Land, L. S., 1983, Application of stable isotopes to studies of origin of dolomite and to problem of diagenesis of clastic sediments, in Arthur, M. A., ed., Stable isotopes in sedimentary geology: SEPM Short Course 10,

p. 4-1 to 4-22.

----- and Prezbindowski, D. R., 1981, The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A.: *Journal of Hydrology*, v. 54, p. 51-74.

Lohmann, K. C., 1987, Geochemical pattern of meteoric diagenetic systems and their application to study of paleokarsts in James N. P., and Choquette, P. W., eds., *Paleokarsts*: Springer-Verlag, p. 58-80.

Lorens, R. B., 1981, Sr, Cd, Mn, and Co distribution coefficients in calcite as a function of calcite precipitation rate: *Geochemica et Cosmochemica Acta*, v. 45, p. 553-561.

Mcree, J. M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale: *Journal Chemistry and Physics*, v.18, p.849-857.

Meendsen, F. C., 1987, Upper Jurassic stratigraphy, porosity distribution, and hydrocarbon potential of eastern southeast Mississippi: M. S. Thesis, Louisiana State University, 187 p.

-----, Moore, C. H., Heydari, E., and Sassen, R., 1987, Upper Jurassic depositional system and hydrocarbon potential of southern Mississippi: *Gulf Coast Association of Geological Societies Transactions*, v. 37, p. 161-174.

Meyers, W. J., 1974, Carbonate cement stratigraphy of the

Lake Valley Formation (Mississippian) Sacramento Mountains, New Mexico: Journal of Sedimentary Petrology, v. 44, p. 837-861.

----- 1978, Carbonate cements: their regional distribution and interpretation in Mississippian limestones of southwestern New Mexico: Sedimentology, v. 25, p. 371-400.

----- 1980, Compaction in Mississippian skeletal limestones, southwestern New Mexico: Journal of Sedimentary Petrology, v. 50, p. 457-474.

----- and Hill, B. E., 1983, Quantitative studies of compaction in Mississippian skeletal limestones, New Mexico: Journal of Sedimentary Petrology, v. 53, p. 0231-0242.

Mook, W. G., Bommerson, J. C., and Staverman, W. H., 1974, Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide: Earth and Planetary Science Letters, v. 22, p. 169-176.

Moore, C. H., 1984, The upper Smackover of the Gulf rim: Depositional system, diagenesis, porosity evolution and hydrocarbon production, in Ventress, W. P. S., Bebout, D. G., Perkins, R. F., and Moore C. H., eds, The Jurassic of the Gulf Rim: Proceedings of third annual research conference of SEPM, Baton Rouge, Louisiana, p. 283-308.

----- 1985, Upper Jurassic subsurface cement - a

- case history, in Schneidermann, N., and Harris, P. M. eds., Carbonate cements: SEPM Special Publication 36, p. 291-308.
- and Druckman, Y., 1981, Burial diagenesis and porosity evolution, Upper Jurassic Smackover, Arkansas and Louisiana: American Association of Petroleum Geologists Bulletin, v. 65, p. 597-628.
- and Brock, F. C., 1982, Porosity preservation in the upper Smackover (Jurassic) carbonate grainstone, Walker Creek Field, Arkansas: Response of paleophreatic lenses to burial processes- Discussion: Journal of Sedimentary Petrology, v. 52, p. 19-23.
- Chowdhury, A, and Heydari, E., 1986, Variation of ooid mineralogy in Jurassic Smackover limestone as control of ultimate diagenetic potential: American Association of Petroleum Geologists Bulletin: v. 70, p. 622-628.
- Mucci, A., and Morse, J. W., 1983, The incorporation of Mg^{+2} and Sr^{+2} into calcite overgrowths: Influence of growth rate and solution composition: Geochimica et Cosmochimica Acta, v. 47, p. 217-233.
- Neimann, J. C., and Read, J. F., 1988, Regional cementation from unconformity-recharged aquifer and burial fluids, Mississippian Newman Limestone, Kentucky: Journal of Sedimentary Petrology, v. 58, p. 688-705.
- Nelson, R. A., 1981, Significance of fracture sets

- associated with stylolite zones: American Association of Petroleum Geologists Bulletin, v. 65, p. 2417-2425.
- Oehler, J. H., 1984, Carbonate source rocks in the Jurassic Smackover trend of Mississippi, Alabama, and Florida, in Palacas, J. G. ed., Petroleum geochemistry and source rock potential of carbonate rocks: American Association of Petroleum Geologists, Studies in Geology #18, p. 63-70.
- Oglesby, T. W., 1976, A model for the distribution of manganese, iron, and magnesium in authigenic calcite and dolomite cements in the Upper Smackover Formation in eastern Mississippi: Unpublished M. Sc. Thesis, University of Missouri, Columbia, MO, 122pp.
- O'Neil, J. R., Clayton, R. N., and Meyeda, T. K., 1969, Oxygen isotope fractionation in divalent metal carbonates: Journal of Chemistry and Physics, v. 51, p. 5547-5558.
- Oxley, M. L., Minihan, E., and Ridgeway, J. M., 1967, A study of the Jurassic sediments in portions of Mississippi and Alabama: Gulf Coast Associations of Geological Societies Transactions, v. 17, p. 24-48.
- Peryt, T., 1983, Coated Grains: Springer-Verlag, New York, 655 p.
- Phillips, W. J., 1974, The development of vein and rock textures by tensile strain crystallization: Journal of Geological Society of London, v. 130, p. 441-448.

- Pingitore, N. E., 1978, The behavior and Zn^{+2} and Mn^{+2} during carbonate diagenesis: Theory and applications: Journal of Sedimentary Petrology, v. 48, p. 799-814.
- Ramsay, J. G., 1980, The crack-seal mechanism of rock deformation: Nature, v. 284, p. 135-139.
- Rogers, M. A., Mcalarg, J. D., and Bailey, J. L., 1974, Significance of reservoir bitumens to thermal maturation studies, Western Canada basin: American Associations of Petroleum Geologists Bulletin, v. 58, p. 1806-1824.
- Russell, C. W., 1985, A strontium isotope study of oil field brines and associated rocks in southeastern Mississippi: Unpublished M.s. thesis, Florida State University, 176 p.
- Rutter, E. H., 1972, The effects of strain-rate changes on the strength and ductility of Solenhofen Limestone at low temperatures and confining pressures: International Journal of Rock Mechanics and Mining Science, v. 9, p. 183-189.
- Saller, A. H., 1985, Diagenesis of Cenozoic limestones on Enewitalk atoll: Ph. D. dissertation, Louisiana State University, Baton Rouge, Louisiana, 363p.
- Sandberg, P. A., 1983, An oscillating trend in Phanerozoic nonskeletal carbonate mineralogy: Nature, v. 305, p. 19-22.
- Sassen, R., 1988, Geochemistry and carbon isotopic studies

of crude oil destruction, bitumen precipitation, and sulfate reduction in the deep Smackover Formation: Organic Geochemistry, v. 12, p. 351-361.

----- Moore, C. H., Meendsen, F. C., 1987a, Distribution of hydrocarbon source potential in the Jurassic Smackover Formation: Organic Geochemistry, v. 11, p. 379-383.

----- Moore, C. H., Nunn, J. A., Meendsen, F. C., and Heydari, E., 1987b, Geochemical studies of crude oil generation, migration, and destruction in the Mississippi Salt Basin: Gulf Coast Association of Geological Societies Transactions, v. 37, p. 217-224.

----- and Moore, C. H., 1988, Framework of hydrocarbon generation and destruction in eastern Smackover trend: American Associations of Petroleum Geologists Bulletin, v. 72, p. 649-663.

Schlanger, S. O., and Douglas, R. G., 1974, The pelagic ooze-chalk-limestone transition and its implications for marine stratigraphy, in Hsu, K. J., and Jenley, H. C., eds., Pelagic sediments on land and under the sea: International Association of Sedimentologists, Special Publication 1, p. 117-148.

Scholle, P. A., and Halley, R. B., 1985, Burial diagenesis - out of sight, out of mind!, in Schneidermann, N., and Harris, P. M., eds., Carbonate Cements: SEPM Special

Publication 36, p. 309-334.

- Searl, A., 1988, The limitation of "cement stratigraphy" as revealed in some lower Carboniferous oolites from South Wales: *Sedimentary Geology*, v. 57, p. 171-183.
- Sharma, T., and Clayton, R. N., 1965, Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates: *Geochemica et Cosmochemica Acta*, v. 29, p. 1347-1353.
- Sheppard, S. M. F., 1986, Characterization and isotopic variations in natural waters, in Valley, J. W., Taylor, H. P., Jr., and O'Neil, J. R., eds., *Stable isotopes in high temperature geologic processes: Mineralogical Society of America, Reviews in Mineralogy*, v. 16, p. 165-180.
- Swett, K., and Knoll, A. H., 1989, Marine Pisolites from Upper Proterozoic carbonates of East Greenland and Spitsbergen: *Sedimentology*, v., 36, p. 75-93.
- Swirydczuk, K., 1988, Mineralogical control on porosity type in upper Jurassic Smackover ooid grainstones, southern Arkansas and northern Louisiana: *Journal of Sedimentary Petrology*, v. 58, p. 339-347.
- Tan, F. C., and Hudson, J. D., 1974, Isotopic studies on the paleoecology and diagenesis of the Great Estuarine Series (Jurassic) of Scotland: *Scottish Journal of Geology*, v. 2, p. 91-128.
- Tucker, M. E., 1984, Calcitic, aragonitic, and mixed calcitic aragonitic ooids from the mid-Proterozoic Belt

- Supergroup, Montana: *Sedimentology*, v. 31, p. 627-644.
- 1985, Calcitized aragonitic ooids and cements from the late Precambrian Biri Formation of southern Norway: *Sedimentology*, v. 43, p., 67-84.
- Waples, D. W., 1980, Time and temperature in petroleum formation: Application of Lopatin's method to petroleum exploration: American Association of Petroleum Geologists Bulletin, v. 64, p. 916-926.
- Wilkinson, B. H., Owen, R. M., and Carroll, A. R., 1985, Submarine weathering, global eustasy, and carbonate polymorphism in Phanerozoic marine ooids: *Journal of Sedimentary Petrology*, v. 55, p. 171-183.
- Buczynski, C., and Owen, R. M., 1985, Chemical control of carbonate phases: Implications from Upper Pennsylvanian calcite-aragonite ooids of southeastern Kansas: *Journal of Sedimentary Petrology*, v., 54, p. 932-947.
- Wong, P. K., and Oldershaw, A., 1981, Burial cementation in the Devonian Kaybob reef complex, Alberta, Canada: *Journal of Sedimentary Petrology*, v. 51, p. 507-520.
- Wood, M., and Wapler, J. L., 1974, The evolution of the interior Mesozoic basin and the Gulf of Mexico: Gulf Coast Associations of Geological Societies Transactions, v. 24, p. 31-41.
- Woronick, R. E., and Land, L. S., 1985, Late burial diagenesis, Lower Cretaceous Pearsall and Lower Glen

Rose Formations, south Texas, in Schneidermann, N., and Harris, P. M., eds, SEPM Special Publication 36, p. 265-275.

Zempolich, W. G., Wilkinson, B. H., and Lohmann, K. C, 1988, Diagenesis of Late Proterozoic carbonates: the Beck Spring Dolomite of eastern California: Journal of Sedimentary Petrology, v. 58, p. 656-672.

CHAPTER IV

DIAGENESIS GONE SOUR: AN EXAMPLE OF THE DIAGENETIC DESTRUCTION OF A JURASSIC HYDROCARBON RESERVOIR, BLACK CREEK FIELD, MISSISSIPPI SALT BASIN

ABSTRACT

The near surface to deep burial diagenetic history of the Smackover Formation at Black Creek field, Mississippi salt basin, was examined by petrographic and geochemical studies of two conventional cores. The study was conducted to document cementation history, variations in chemical composition of the cements, and porosity evolution of the Smackover Formation during its 6 km burial history.

Early diagenetic events include marine cementation, dolomitization, and chertification. Shallow burial diagenesis includes precipitation of pre-bitumen calcite, saddle dolomite, and anhydrite. These phases postdate physical and chemical compaction features and predate bitumen precipitated due to hydrocarbon destruction (at about 120 °C) suggesting that they formed from near surface temperatures to about 120 °C. Deep burial diagenetic features include calcitization of anhydrite, precipitation of post-bitumen calcite, late silica, fluorite, elemental sulfur, and minor amounts of pyrite. These phases postdate bitumen formation in the reservoir. Regional geologic studies indicate that they are present only where the Smackover Formation is buried to over 19,000 ft (5,795 m) and has been subjected to temperatures of greater than 150 °C.

Both shallow and deep burial calcite cements have similar $\delta^{18}\text{O}$ compositions (-5) despite formation at

significantly different temperatures. Their strontium isotopic values (0.7070) are similar to Late Jurassic sea water. These data suggest that cementation occurred in a closed system. The $\delta^{13}\text{C}$ compositions of pre-bitumen calcite cements are similar to that of the host carbonate rock (+4), while those of post-bitumen calcite cements range from -2 to -17 suggesting incorporation of carbon derived from thermal oxidation of hydrocarbon gases.

Pre-bitumen calcite cements contain 100 ppm Sr, 2800 ppm Mg, 56 ppm Fe, and 60 ppm Mn. Post-bitumen calcite cements have 1031 ppm Sr, 1071 ppm Mg, <1 ppm Fe, and 68 ppm Mn. The variations of trace element compositions of calcite cements suggest that during burial the Sr/Ca ratio of pore waters increased, the Mg/Ca ratio decreased, Fe was removed, and the Mn/Ca ratio did not change significantly.

Cementation and bulk volume reduction caused total destruction of intergranular pores in grainstone portion of the limestone intervals with the present porosity of about <0.1%. Undolomitized grainstone samples contain an average of 1.3% marine cement, 7.8% pre-bitumen calcite cement, 1.1% saddle dolomite, 2.5% replacement anhydrite, 1.6% bitumen, and 5.0% post-bitumen calcite cement. The total cement of grainstones range from 5% to 35.3%. Assuming that grainstones originally contained 45% pore volume, an average of 17% of the 45% is lost by cementation and the remain by bulk volume reduction. Dolomite samples, however, retain

significant intercrystalline porosity (1-20%) and permeability (1-60 millidarcy). Dolomite samples contain an average of 12.9% bitumen, 9.3% post-bitumen calcite, 6.9% thin section porosity, and 0.5% fluorite.

Reaction of sulfates with H_2S produced elemental sulfur which reacted with hydrocarbons generating more H_2S in a self enforcing cycle. Lack of metal ions to stabilize H_2S , availability of sulfates, and closed system preventing escape of generated H_2S resulted in destruction of virtually all of hydrocarbons in this reservoir.

INTRODUCTION

Porosity evolution and cementation history of carbonate rocks during burial diagenesis has been a subject of some concern for a number of years (Scholle and Halley, 1985; Moore, 1989). Most of our observations of burial diagenetic studies have, however, been restricted by the relatively shallow depth (3,000 m to 4,000 m) of the hydrocarbon reservoirs, and exploration targets that furnish the bulk of the available study materials (Moore and Druckman, 1981; Moore, 1985; Halley, 1985). As a result, most burial diagenetic studies describe diagenetic events that occur either prior to, or during hydrocarbon migration into the reservoir, or diagenetic environments that exhibit relatively moderate temperature and pressure conditions. There are some notable exceptions, however, such as the deep

Stuart City trend in south Texas as described by Prezbindowski (1985); the upper Jurassic Smackover of Alabama studied by Feazel (1985); and the Ordovician of southeastern New Mexico reported by Lee and Friedman (1987). However, the deep burial diagenetic processes and products presented here were not reported in the cited investigations.

Cores from a Jurassic Smackover reservoir at Black Creek field, in southern Mississippi, retrieved from a burial depth of over 19,000 ft (5,795 m) and subjected to bottom hole temperatures in excess of 200 °C, provide an excellent opportunity to document deep burial diagenetic processes that are seldom encountered in most carbonate exploration activities. The Black Creek field produced only H₂S, CO₂ and minor amounts of methane from porous dolomite and was abandoned shortly after discovery (Grizzaffi and Thompson, 1970). The gas composition, and the presence of extensive pyrobitumen in the reservoir rocks suggests that Black Creek was an oil field that was subsequently destroyed during progressive deep burial in the Mississippi salt basin (Sassen and Moore, 1988; Heydari and Moore, 1989).

The present paper documents the sequence of diagenetic events that affected the Jurassic Smackover Formation and the impact of these events on porosity as the sequence has been progressively buried into the deep subsurface at Black Creek field. An important, and unique facet of the story is

the role that diagenesis played in the ultimate destruction of the hydrocarbons trapped in the Black Creek reservoirs.

It is anticipated that in the future our search for greater gas reserves will lead to much deeper drilling in carbonate as well as siliciclastic dominated basins and that understanding diagenesis and porosity evolution associated with these deep, high temperature, and high pressure processes will become increasingly more important.

The purpose of this study is to document the petrographic and geochemical characteristics of diagenetic phases present in the Smackover Formation in order to evaluate processes of porosity evolution and hydrocarbon destruction in this deep reservoir. This is done by describing the diagenetic history and porosity evolution of the Smackover Formation during three stages of diagenesis: early pre-burial, shallow burial, and deep burial. The importance of deep burial diagenetic processes and products are specially emphasized. This diagenetic realm has not been investigated in previous burial diagenetic studies (Bathurst, 1980, 1986; Wanless, 1983; Halley, 1984, 1985; Scholle and Halley, 1985; Choquette and James, 1986), although, a brief review was presented by Moore (1989).

ANALYTICAL METHODS

Petrographic observations were made on polished and half-stained with Alizarine red-s and potassium ferricyanide

(Dickson, 1966) thin-sections. Cathodoluminescence (CL) observations were performed with a Technosyn luminescope. Operating conditions were 15 kv gun potential, focused beam diameter of one centimeter, 0.5 millitorr vacuum, and 300-400 μ A beam current. Scanning electron microscopy (SEM) was performed on gold coated samples with a JEOL T-300 electron microscope. Point counting data are the result of 600 points counted on each thin section.

Sampling of cements and allochems for chemical analyses was accomplished by crushing the rock and separating cements and allochems under a binocular microscope. Respective samples were stained slightly with Alizarine red-s and handpicked to separate impurities. They were then washed with 0.05 N HCl to remove the stain and rinsed with distilled and deionized water three to five times. When mechanical separation was not possible the core slabs were polished to 0.3 microns and calcites were drilled out with a Jensen milling machine. Separated samples were powdered in an agate mortar and pestle. The powdered samples were analyzed by X-ray diffraction from 20 to 32 degrees 2θ using $\text{CuK}\alpha$ radiation to detect 100% reflection peaks of dolomite, anhydrite, calcite, celestite, and strontianite. Only mineralogically pure samples were chosen for chemical analyses.

Trace element analyses of the samples were performed by dissolving 100 mg of sample in 0.5 N HCl. The leachate was

passed through a 45 μm millipore filter and its volume was raised to 100 mL by adding 0.5 N HCl. Trace elemental analyses were conducted by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP). The relative precision of the analyses is 2.5% for Mg, 0.8% for Sr, 4.7% for Fe, and 7.9% for Mn. The detection limit for all elements is <1 ppm.

Oxygen and carbon isotopic analyses of carbonates were performed by the Coastal Science Lab, Austin, Texas, by reacting the carbonates with 100% orthophosphoric acid (McRea, 1950). The results are reported in ‰ relative to PDB (Peedee belemnite) standard with a precision of ± 0.2 ‰. The $\delta^{18}\text{O}$ compositions of dolomites reported in this paper are not corrected for phosphoric acid fractionation (Sharma and Clayton, 1965).

The strontium isotopic analyses of allochems were performed by Dr. R. Koepnick of the Mobil Field Research Lab at Dallas and analyses of cements by Dr. L. S. Land of the University of Texas at Austin. The Sr extraction was accomplished by common ion exchange method. The precision of the analyses is ± 0.00005 .

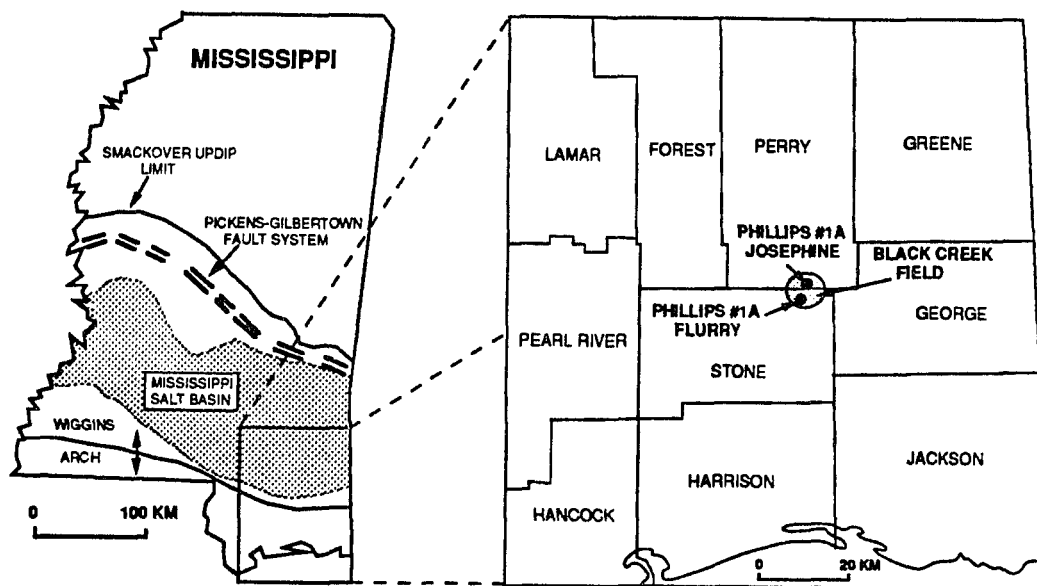
Oxygen isotope composition of quartz was measured by Dr. L. S. Land using a method described by Dutton and Land (1988). The results are reported in ‰ relative to SMOW (standard mean ocean water). The precision of analyses is ± 0.2 ‰.

GEOLOGIC SETTING OF BLACK CREEK FIELD

Black Creek field is located on the northern flank of the Wiggins arch (Fig. 4.1), near the southern margin of the Mississippi salt basin. This basin is one of four interior salt basins formed as a result of extension associated with the opening of the main Gulf of Mexico during early Mesozoic (Wood and Walper, 1974; Buffler and Sawyer, 1985). The Mississippi salt basin is the largest and perhaps the best known of these basins and it is separated from the main body of the Gulf of Mexico by the Wiggins Arch. It is bounded on the north by the Pickens-Gilbertown fault system (Fig. 4.1).

Jurassic lithofacies in the Mississippi salt basin from oldest to youngest include siliciclastics and evaporites of the Werner Formation, Louann Salt, siliciclastics of the Norphlet Formation, carbonate of the Smackover Formation, carbonates and evaporites of the Haynesville Formation, and siliciclastics of the Schuler Formation (Oxley et al., 1967; Dinkins, 1968; Badon, 1974; Meendsen et al., 1987; Eldridge, 1989). The Smackover Formation is a marine unit of Oxfordian age (Imlay 1980) deposited in and along the margins of the salt basins. It overlies the siliciclastic deposits of the Norphlet Formation and is overlain by carbonates and evaporites of the Haynesville Formation. However, the Norphlet Formation is not present at Black Creek field. At this location, the Smackover Formation overlies 1 ft of marine reworked sandstone and 5 ft of the Pine Hill

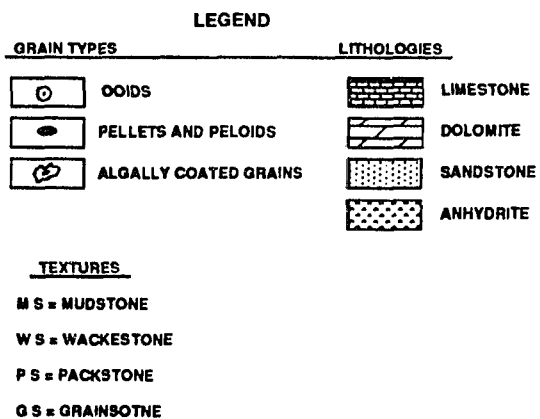
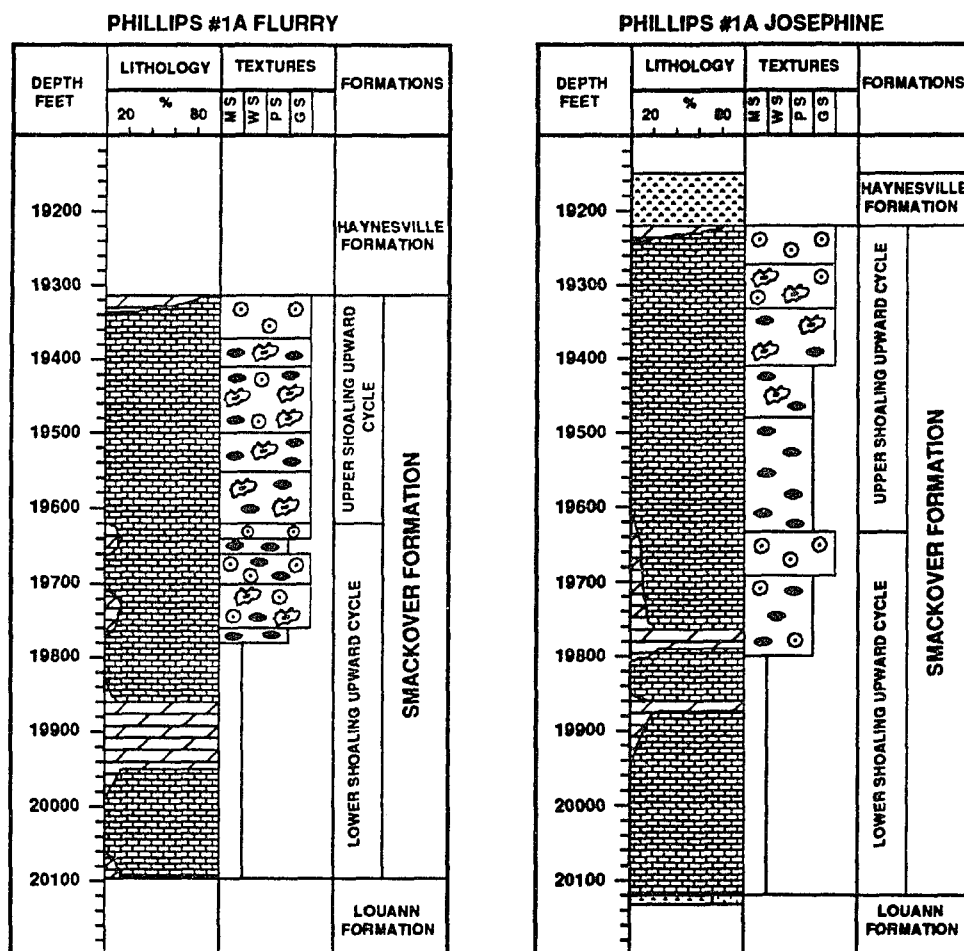
Figure 4.1. Regional geologic map showing the location of Black Creek Field, Phillips #1A Josephine, and Phillips #1 Flurry wells.



Anhydrite member of the Louann Group (Wakelyn, 1979) (Fig. 4.2). Two deep wells, the Phillips #1A Josephine and the Phillips #1A Flurry, cored the entire thickness of the Smackover Formation at Black Creek field. The Josephine well was cored from 19,148 ft to 20,150 ft (5,840 m to 6,146 m) and had a corrected (using correction curve of Kehle, 1971) bottom hole temperature of 195 °C. The cored interval of the Flurry well is 19,250 ft to 20,210 ft (5,871 m to 6,164 m) and its corrected bottom hole temperature is 205 °C. No liquid hydrocarbons and no significant hydrocarbon gases have been produced from the Smackover Formation along this area of the Wiggins arch (Long, 1978). Gases from Black Creek field, for example, contain 78% H₂S, 20% CO₂, and 2% CH₄ (Grizzaffi and Thompson, 1970; Parker, 1974). Given the fact that the Smackover reservoir is within the dry gas window at this field and the reservoir temperature is below thermal destruction of methane (400 °C, Takach et al., 1987), the lack of hydrocarbon gases in Black Creek field requires explanation.

The Smackover Formation at Black Creek field is composed of two shoaling upward cycles (Fig. 4.2). In the Phillips #1A Josephine, the lower cycle consists of a basal extremely well laminated mudstone member about 30 ft (9 m) thick, a middle laminated and borrowed mudstone member about 300 ft (91 m) thick and an upper grainstone-packstone member about 200 ft (61 m) thick. The upper cycle is composed of a

Figure 4.2. Stratigraphic description of cored upper Jurassic lithologies in Phillips #1A Josephine and Phillips #1A Flurry wells, Black Creek field, Mississippi salt basin.



lower wackestone-packstone member and an upper oolitic grainstone member, each about 200 ft (61 m) thick. In the Phillips #1A Flurry, the lower cycle is similar to the one in the Josephine well (Fig. 4.2). However, the upper cycle is composed on a lower oncolite-peloid dominated grainstone member and an upper ooid grainstone member (Fig. 4.2). The basal laminated member of the lower cycle was deposited below wave base in a stagnant (anoxic) and possibly hypersaline environment (Meendsen et al., 1987; Eldridge, 1989). The middle member of the lower cycle formed below wave base; Grainstone members of each cycle formed in a shallow, high-energy environment possibly associated with a salt structure (Meendsen et al., 1987; Eldridge, 1989). The uppermost 100 ft (30 m) of the middle mudstone member of the lower cycle is extensively dolomitized in the Flurry well and partially dolomitized in the Josephine well (Fig. 4.2). Organic geochemical studies (Sassen et al., 1987 a,b) suggest that the laminated rocks are the source of hydrocarbons in the upper Smackover reservoir.

Core lab porosity and permeability analyses and thin section studies indicate that the only lithofacies that is still porous and permeable is the dolomite. All of the primary intergranular porosity in grainstone facies of the Smackover Formation are lost due to cementation and bulk volume reduction during burial. The grainstone lithofacies in the shallower portion of the Mississippi salt basin at

depths of 13,000 to 15,000 ft (3,965 m to 4,575 m) contains 5-10% porosity.

Thermal maturities calculated from the burial history curve of the Smackover Formation in this field (Fig. 4.3) indicate that the onset of hydrocarbon maturation and migration occurred at a depth of approximately 11,000 ft (3,355 m) at the end of the Early Cretaceous and continued to 14,000 ft (4,270 m) of burial. Destruction of liquid hydrocarbons and generation of hydrocarbon gases, H_2S , and solid bitumen began at about 14,000 ft (4,270 m), during the Late Cretaceous, and continued until the present time.

Wakelyn (1977) and Eldridge (1989) presented detailed lithofacies descriptions and depositional setting of the Smackover at Black Creek field. Recently, McLimans (1987) reported fluid inclusion analyses of calcite cements from the Josephine well that contain sulfur, H_2S (90%), and methane (10%). His data suggest that water and sulfur were entrapped at a temperature of about 260 °C and a pressure equivalent to 5,800 m burial depth.

EARLY PRE-BURIAL DIAGENESIS AND POROSITY EVOLUTION

This diagenetic realm encompasses events affecting the sediments during and soon after deposition. The most important early pre-burial diagenetic events include marine cementation, dolomitization, and chertification (Fig. 4.4). The marine cements are composed of isopachous fibrous low

Figure 4.3. Burial history curve for the top of the Smackover Formation reconstructed from the compacted thickness of sediments penetrated the Phillips #1A Josephine well. Vitrinite reflectances (R_o) are estimated from calculated time temperature indices (Waples, 1980).

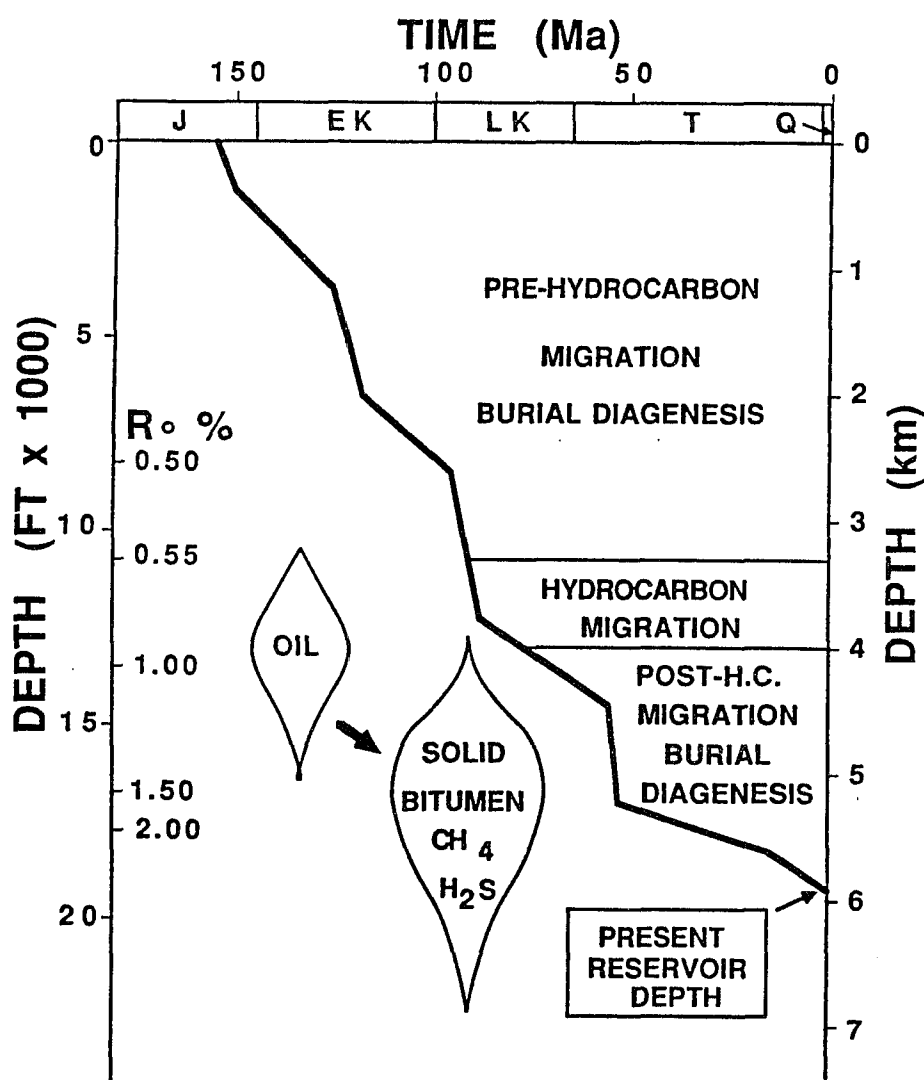
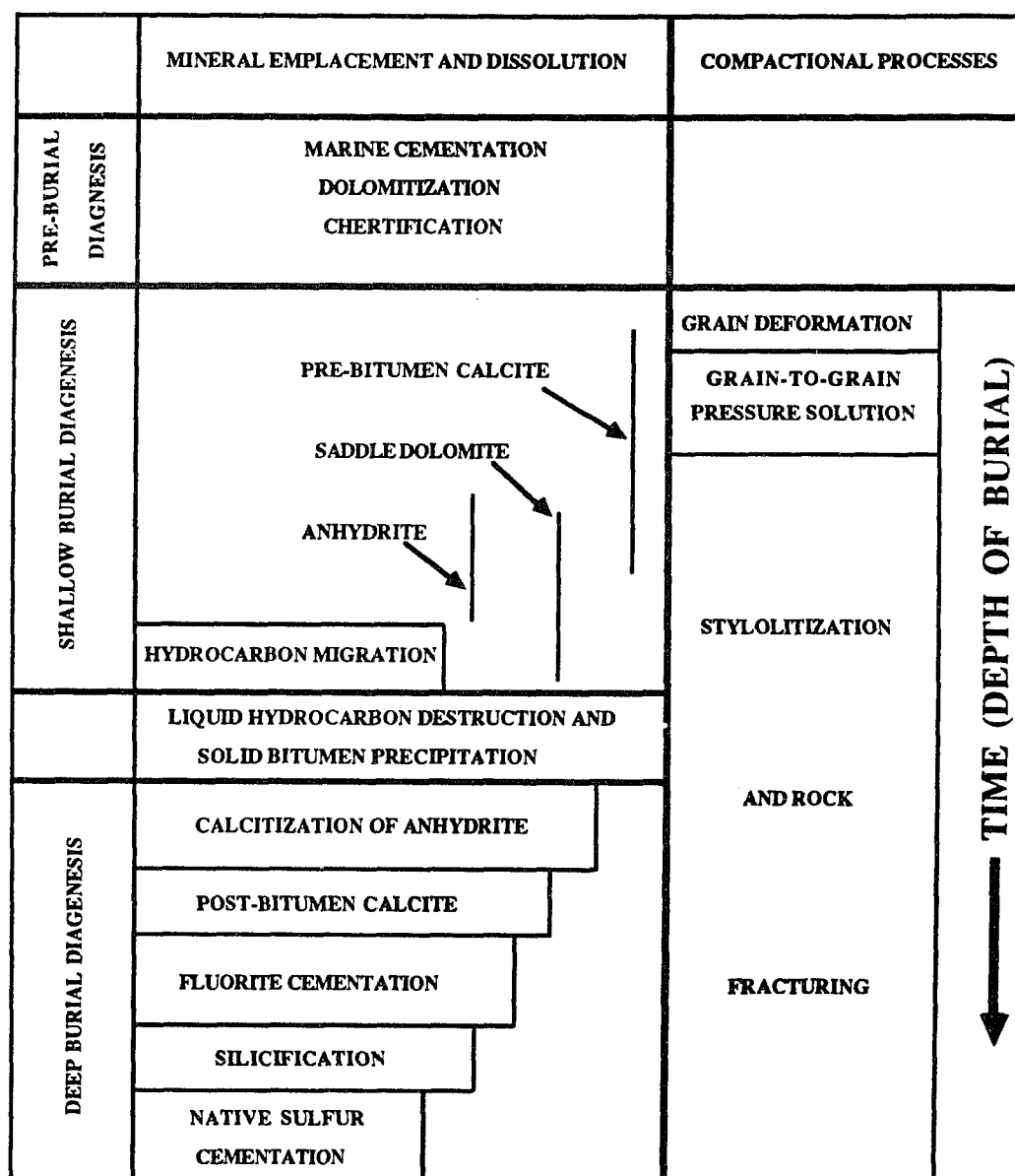


Figure 4.4. Paragenetic sequence of the Smackover Formation, Black Creek field, Mississippi salt basin.



Mg-calcite cement which coats ooids, algal coated grains, and other allochems (Fig. 4.5) in the grainstone portion of both wells.

A dolomitization event affected the formation and formed an important, porous dolomite zone in the field (Fig. 4.2). In the Flurry well, the dolomite is composed of numerous second order shoaling-upward cycles, each starting with a laminated mudstone and ending with a layer of grainstone and/or breccia. The breccia layers contain fragments of various lithologies. This suggests that they may have formed during exposures or during storm events. In addition, the dolomites contain cavities resembling dissolved evaporite nodules which suggests that the breccia layers may represent evaporite solution of collapse breccia. In either case, it is believed that the dolomitization and formation of breccia are ultimately related. This evidence as well as the low density of the dolomitized grains plus the presence of dolomitized fragments in the associated breccia suggest that dolomitization occurred early. The average Sr, Fe, Mn, and Na contents of the dolomite in ppm are 62, 10, 90 and 212, respectively (Table 4.1). Their $\delta^{18}\text{O}$ values range from -2.6 to -5.2 with an average of -3.2. Their $\delta^{13}\text{C}$ values range from +2.3 to +5.5 with an average of +4.8 (Table 4.1). The origin of the dolomite is not clear at this time and will be the subject of a subsequent investigation. Dolomitization was possibly accomplished by

Figure 4.5. Plain light photomicrograph showing isopachous marine cement (MC) pore fill calcite cement (C). Note deformation twinning in pore fill cement. Phillips #1A Josephine 19,370 ft (5908 m).

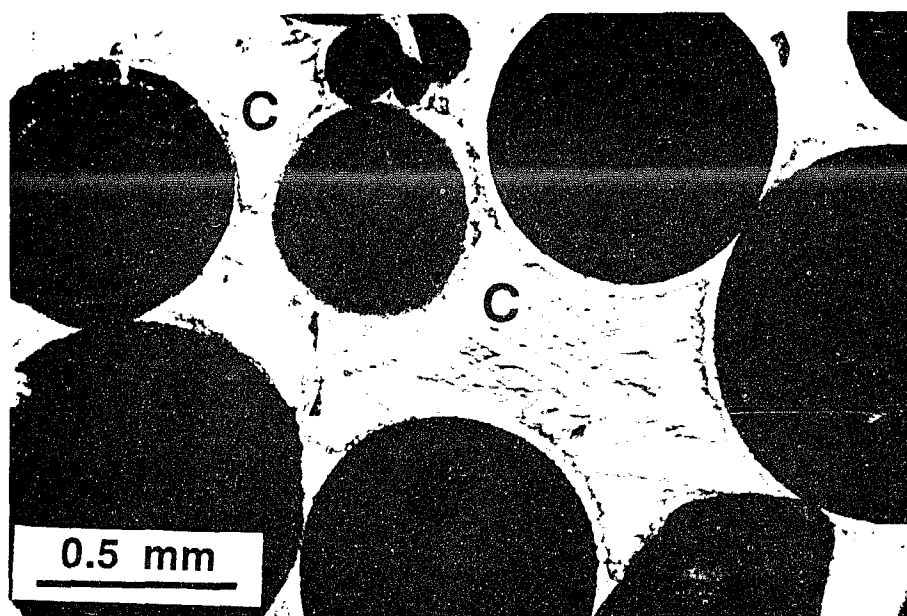


Table 4.1. Trace element (in ppm), stable oxygen and carbon isotopic (relative to PDB) composition of dolomite in Black Creek field. PF: Phillips #1A Flurry.

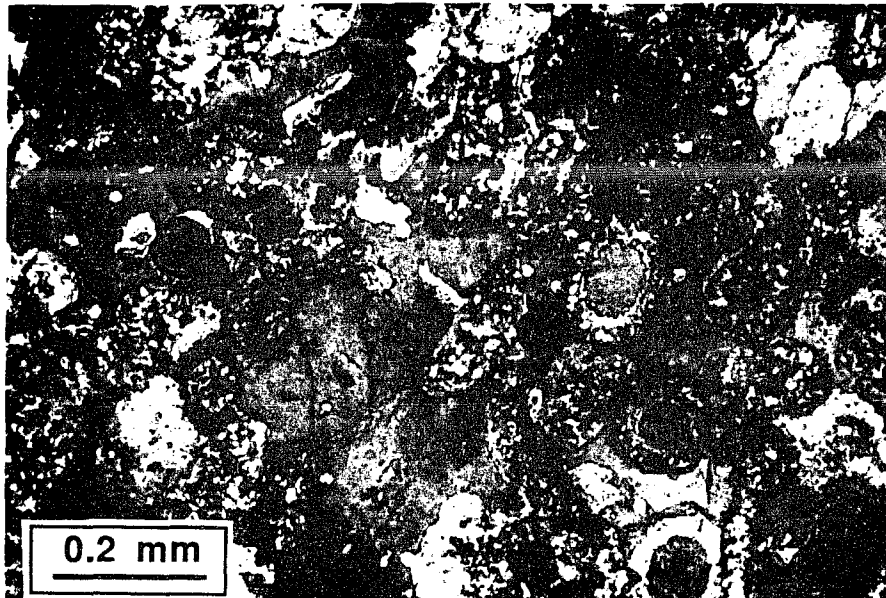
Depth (ft)	Sr	Fe	Mn	Na	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
PF19880	64	6	59	308	-5.2	+5.2	
PF19885	62	1	44	225	-2.9	+5.2	
PF19890	62	2	45	155	-2.6	+5.1	
PF19895	71	8	49	171	-3.1	+4.7	
PF19900	61	3	59	203	-2.8	+5.0	
PF19905	66	15	90	704	-2.9	+4.7	
PF19910	49	19	133	216	-2.6	+5.2	
PF19920	63	13	85	256	-2.9	+5.5	
PF19925	56	31	109	192	-3.9	+5.0	
PF19938	75	7	124	212	-2.6	+2.3	
PF19942	56	9	197	187	-3.5	+5.1	

normal sea water. The trace elements as well as isotopic composition of the dolomite support this interpretation. Smackover dolomites with similar isotopic compositions from Alabama (Saller and Moore, 1986) and Florida (Vinet, 1984) are also interpreted as early marine dolomites.

Abundant chert nodules are present in the grainstone member of the lower shoaling-upward cycle, particularly in the Josephine well. Chert replaces ooids and peloids. The low grain density of the allochems imbedded within chert nodules and the absence of chertified late cements (Fig. 4.6) suggest that chertification took place relatively early. The source of silica and the mechanism of chertification are not clear. One possible source of silica is the dissolution and mobilization of siliceous sponge spicules in adjacent low energy mudstones of the Smackover Formation and later precipitation to form more stable microcrystalline quartz or chert. Sponge spicules are abundant in mudstone facies of the Smackover Formation in Alabama and Florida (Vinet, 1990, personal communication). There is no evidence of exposure or evaporite formation in the section where chert nodules occur. Therefore, formation of chert in association with evaporites or marine-fresh-water mixing (Knauth, 1981) is unlikely.

It is assumed the grainstones of the Smackover Formation, similar to grainstones from modern marine environments (Enos and Sawatsky, 1981), originally contained

Figure 4.6. Plain light photomicrograph showing chertified allochems. Stained with alizarine red-s. Phillips #1A Josephine 19,649 ft (5993 m).



about 45% porosity. Since no grain dissolution is observed in grainstones in Black Creek field, it is clear that the only porosity type present upon burial was intergranular. Marine cements are present only as thin isopachous coatings. Only 10 out of 42 grainstone samples that were point counted contain circum granular marine cement. In these samples marine cement range from 0.2% to 16.6% (Table 4.2). These samples, therefore, were buried with most of their porosities still open. The remaining 32 grainstone samples were buried with all of their original 45% porosity uncemented. The dolomite contained intercrystalline and vuggy porosities. Dolomite is assumed to have had a pre-burial porosity of near 50%, similar to pervasively dolomitized rocks of the Florida platform (Schmoker and Halley, 1982). Dolomites do not show any cement prior to precipitation of bitumen after hydrocarbon migration. Therefore, the dolomites were buried with all of their 50% porosity intact.

SHALLOW BURIAL DIAGENESIS AND POROSITY EVOLUTION

In the Mississippi salt basin, this realm of diagenesis includes diagenetic process taking place from the initiation of burial to about 15,000 ft (4,575 m) and a temperature range of 25-120 °C. Lack of early cements, other than as marine cements, in the majority of grainstones from Black Creek suggests that these rock were buried as loose grains

Table 4.2. Point counting data reporting concentrations of grains (G), marine cement (M C), pre-bitumen calcite cement (PRBC), saddle dolomite (S D), anhydrite (A), bitumen (B), post-bitumen calcite cement (PBC), and porosity (P) in grainstones in Black Creek field. Sample # indicate depth of sample in feet. PF stands for Phillips #1A Flurry and PJ for Phillips #1A Josephine. T C represents total cements. Total cement is calculated assuming anhydrites were grains because anhydrite occurs as replacements of grains not as cement.

Table 4.2.

SAMPLE #	% G	% M C	%PRBC	% S. D.	% A	% B	% PBC	% P	% T C
PJ19241	95.0	0.0	4.7	0.3	0.0	0.0	0.0	0	5.0
PJ19245	90.4	0.0	4.5	0.8	0.0	0.0	4.3	0	9.6
PJ19250	81.1	0.0	6.7	0.0	0.3	4.4	7.5	0	18.6
PJ19257	75.0	0.0	15.7	0.6	2.4	4.2	2.1	0	23.2
PJ19270	64.8	16.6	18.7	0.0	0.0	0.0	0.0	0	35.3
PJ19277	85.3	0.0	12.7	1.4	0.7	0.0	0.0	0	14.1
PJ19278	77.3	0.0	18.5	1.7	0.7	0.0	1.8	0	22.1
PJ19279	83.7	0.0	13.6	0.3	0.0	0.0	2.4	0	16.3
PJ19280	81.9	4.0	9.6	0.0	0.0	0.0	4.6	0	18.1
PJ19283	86.3	0.0	8.3	0.0	0.0	0.0	5.4	0	13.7
PJ19286	78.4	0.3	11.5	0.0	0.0	0.0	9.8	0	21.6
PJ19289	73.3	0.0	17.7	0.0	0.0	0.0	9.0	0	26.7
PJ19296	89.2	0.0	8.6	0.0	0.0	0.0	2.2	0	10.8
PJ19310	90.9	0.2	8.9	0.0	0.0	0.0	0.0	0	9.1
PJ19315	83.9	0.0	4.9	0.0	0.0	0.3	10.9	0	16.1
PJ19323	86.4	0.0	1.1	0.0	0.6	0.0	11.9	0	13.1
PJ19326	85.1	0.0	1.9	0.0	1.3	1.7	10.0	0	13.8
PJ19340	86.3	0.0	7.6	2.5	2.2	0.0	1.5	0	11.8
PJ19345	76.1	0.0	2.3	8.8	4.5	0.0	8.3	0	20.3
PJ19348	81.4	0.0	1.6	5.1	1.5	0.0	10.4	0	17.3
PJ19349	75.0	0.0	2.5	2.5	10.6	0.0	9.3	0	16.1
PJ19350	78.9	0.0	2.6	1.8	7.3	0.0	9.4	0	14.9
PJ19351	78.7	0.0	2.7	4.7	5.5	0.0	8.4	0	16.7
PJ19355	78.3	0.0	3.1	4.2	5.8	0.0	8.5	0	25.0
PJ19360	91.2	0.0	1.9	1.0	0.0	0.9	5.0	0	8.8
PJ19362	87.2	0.0	2.7	3.0	0.0	0.8	6.2	0	12.8
PJ19370	54.4	0.0	3.1	1.0	39.6	0.0	1.9	0	9.9
PJ19380	76.3	0.0	5.0	2.2	11.9	0.0	4.7	0	13.4
PF19325	86.8	0.0	13.2	0.0	0.0	0.0	0.0	0	13.2
PF19327	89.4	0.0	10.6	0.0	0.0	0.0	0.0	0	10.6
PF19331	86.9	0.0	2.8	0.0	0.0	6.0	4.4	0	13.1
PF19341	70.3	0.0	8.9	0.0	0.0	18.4	2.5	0	29.7
PF19355	81.2	0.0	9.6	0.0	0.0	2.3	6.9	0	18.8
PF19370	88.4	0.0	6.8	2.4	0.0	0.0	2.4	0	11.6
PF19377	74.2	3.9	16.5	0.0	0.0	0.0	5.5	0	25.8
PF19411	79.9	0.0	10.2	0.0	0.0	1.9	8.0	0	20.1
PF19425	81.5	0.5	10.8	0.0	0.0	1.6	5.6	0	18.5
PF19435	76.3	3.3	6.1	1.2	0.0	7.8	5.3	0	23.7
PF19450	83.8	1.0	8.4	0.0	0.0	1.0	5.8	0	16.2
PF19455	82.9	1.0	7.3	0.0	0.0	3.2	5.6	0	17.1
PF19710	71.5	10.7	9.4	0.6	4.5	2.3	1.2	0	25.2
PF19711	64.5	12.9	5.9	0.3	4.4	10.0	2.0	0	32.5
AVERAGE	80.7	1.3	7.8	1.1	2.5	1.6	5.0	0	17.4

with essentially all of their intergranular porosity intact. Burial pressure resulted in physical and chemical compaction. Calcium carbonate released by pressure solution along grain contacts and stylolites precipitated as cements in intergranular pores. The cements include pre-bitumen calcite followed by saddle dolomite and late anhydrite (Fig. 4.4). Migration of liquid hydrocarbons ended diagenesis in the oil wet reservoirs. Diagenesis, however, continued in the water wet rocks. Initiation of thermal destruction of hydrocarbons and precipitation of solid bitumen ended the formation of these phases and therefore shallow burial diagenesis.

Pre-Bitumen Calcite Cements

Thin section photomicrographs demonstrate that pre-bitumen calcite cements postdate grain deformation and grain-to-grain pressure solution (Fig. 4.7), while predating bitumen precipitation (Fig. 4.8). Pre-bitumen calcite occurs as coarse crystalline mosaic or poikilitic cement ranging in size from 0.1 mm to 0.5 mm. Figure 4.8 illustrates distinctive petrographic characteristics of pre-and post-bitumen calcite cements. Pre-bitumen calcite cement prevented the surfaces of allochems from being coated by bitumen. In addition, the interface between the pre-bitumen calcite cement and bitumen is very sharp, indicating that bitumen conformed to the crystal faces of the pre-existing

Figure 4.7. Photomicrographs showing pre-bitumen calcite cement postdates grain fracturing and grain-to-grain pressure solution. Phillips #1A Josephine, 19,277 ft (5,879 m). SD: Saddle dolomite.

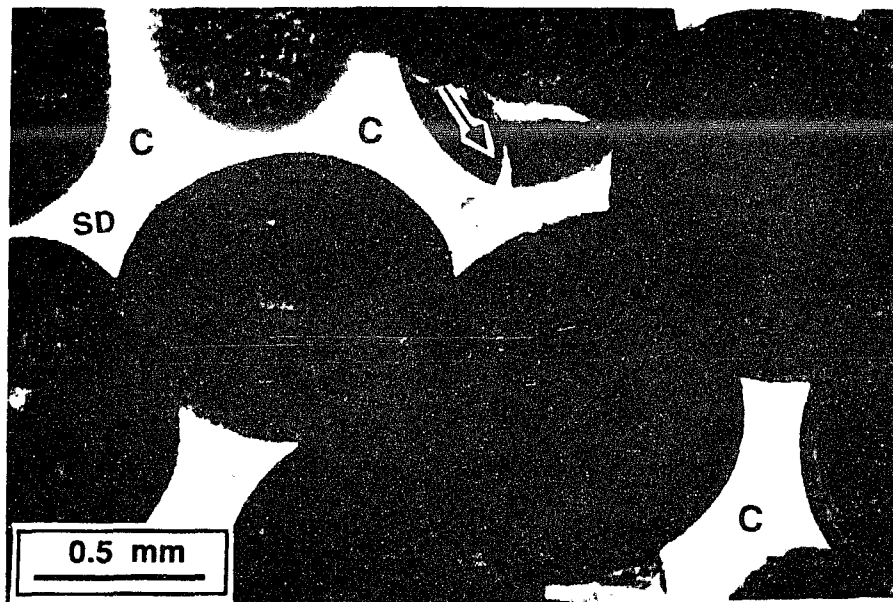


Figure 4.8. Photomicrograph of pre- and post-bitumen calcite cements. The large calcite cement in the center of the photograph precipitated prior to bitumen emplacement. Note that the allochems that this calcite grew from are devoid of bitumen coating and the calcite intersects bitumen along sharp euhedral crystal faces. The smaller calcite in the bottom center of the photograph is a post-bitumen calcite. Phillips #1A Flurry, 19,711 ft (6,012 m).

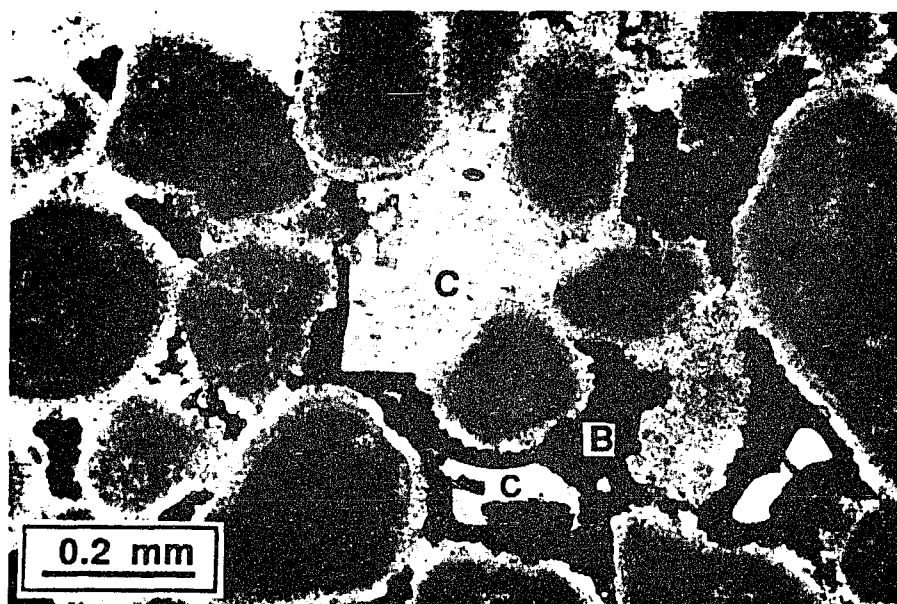
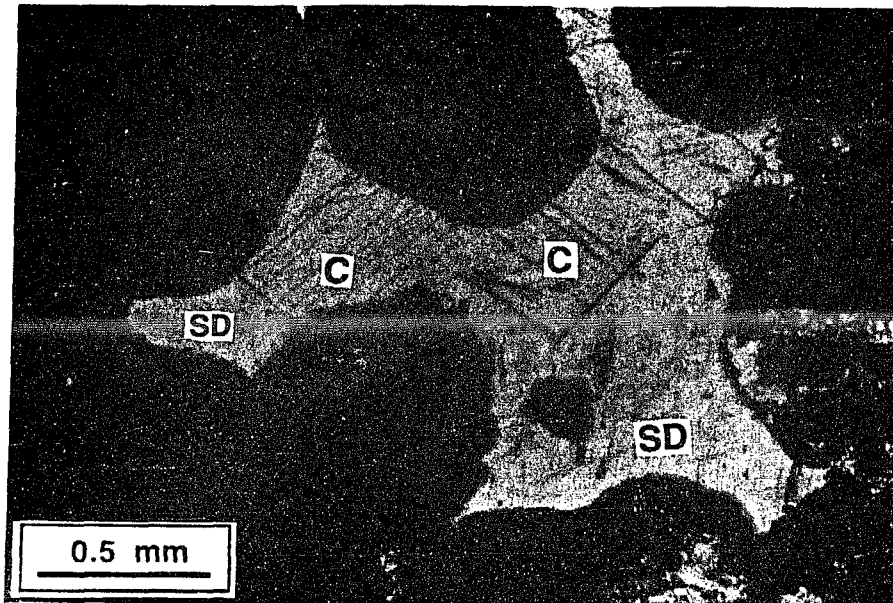
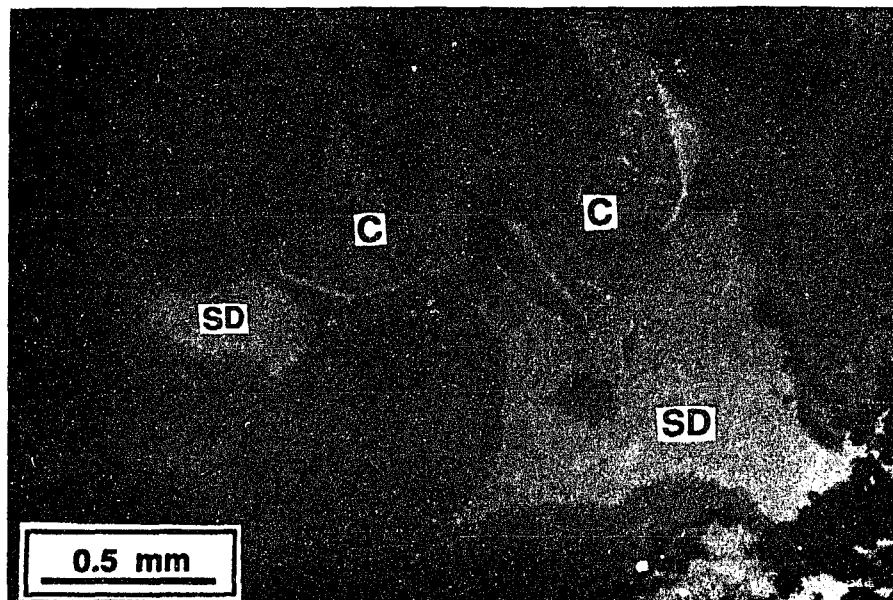


Figure 4.9. (A) Plain light and (B) cathodoluminescence photomicrograph showing saddle dolomite (SD) which postdates calcite cement (C). Calcite shows dull luminescent zonation. Zones 2, 3, and 4 are present. Saddle dolomite is very dull luminescent and unzoned. Phillips #1A Josephine 19,348 ft (5,901 m).

Figure 4.9.



A



B

calcite cement. Pre-bitumen calcite exhibits luminescent zonation. All zones, however, are dully luminescent (Fig. 4.9B). These cements show deformation twinning (Fig. 4.5), possibly formed simply due to high overburden pressures occasioned by deep burial, because the area has not been influenced by significant tectonic stress.

The bulk $\delta^{18}\text{O}$ composition of the pre-bitumen calcite cement ranges from -4.71 to -7.1 with an average of -5.3. Their $\delta^{13}\text{C}$ composition ranges from +4 to +6 with an average of +4.6 (Table 4.3, Fig. 4.10). The strontium isotopic composition of bulk pre-hydrocarbon migration calcite cement is 0.70693 (Table 4.3, Fig. 4.11). The calcite cements contain 103 ppm Sr, 2842 ppm Mg, 50 ppm Fe, and 36 ppm Mn (Table 4.3).

The average $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ compositions of allochems (ooids and algally coated grains) and mudstones are -3.1 and +3.8, respectively (Table 4.4, Fig. 4.10). The strontium isotopic composition of allochems and mudstones is 0.70696 (Table 4.4, Fig. 4.11). Allochems contain an average of 3642 ppm Mg, 332 ppm Sr, 51 ppm Fe, and 21 ppm Mn (Table 4.4).

Saddle Dolomite and Late Anhydrite

Saddle dolomite exhibits very dull luminescence and is unzoned (Fig. 4.9). It generally postdates pre-bitumen calcite cement. The $\delta^{18}\text{O}$ compositions of the saddle dolomite range from -1.1 to -2.1 with an average of -1.5. Its $\delta^{13}\text{C}$

Table 4.3. Trace element (in ppm), stable oxygen and carbon isotopes (relative to PDB), and strontium isotopic composition of shallow burial cements. PF: Phillips #1A Flurry; PJ: Phillips #1A Josephine.

Depth (ft)	Mg	Sr	Fe	Mn	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Calcite Cement							
PJ19270					-5.0	4.8	
PJ19273	2482	112	38	30	-4.6	4.7	0.70699
PJ19276	3410	100	54	54	-4.9	5.0	
PJ19280	2995	104	39	39	-5.1	3.5	0.70692
PJ19289	3072	102	43	36	-4.7	6.0	
PF19311	2354	88	74	23	-7.1	4.1	0.70695
PF19450	2742	112	49	32	-5.5	4.0	0.70687
Saddle Dolomite							
PJ19330					-1.1	5.0	
PJ19332					-1.5	5.3	0.70693
PJ19351					-2.1	5.0	
PJ19352					-1.4	2.6	

Figure 4.10. Carbon-oxygen isotope plot of allochems and pre-bitumen calcite, and saddle dolomite.

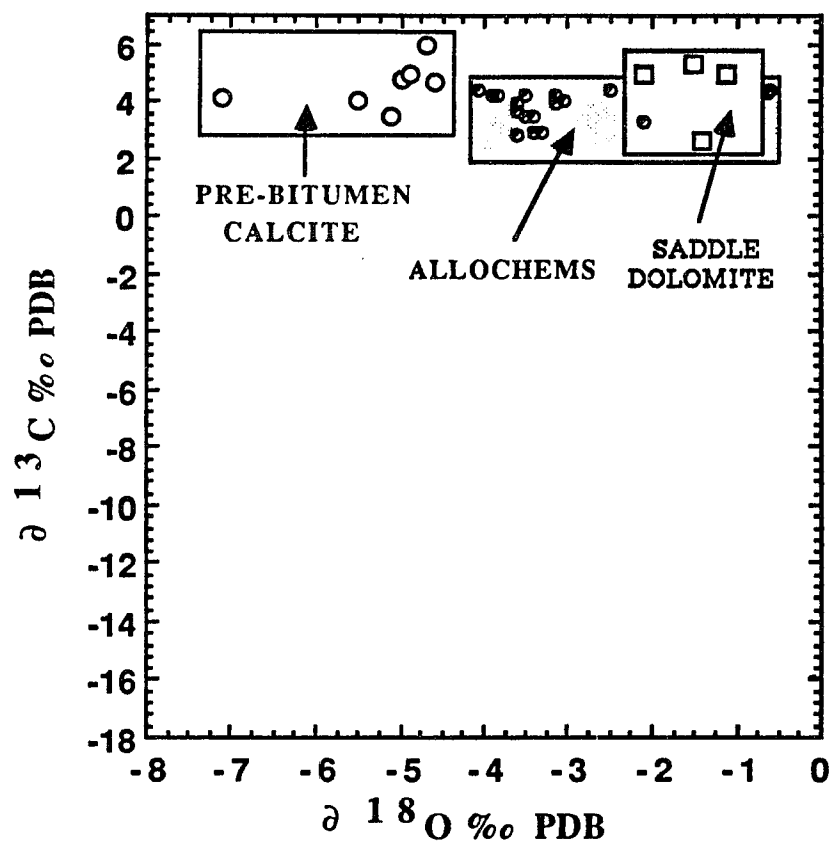


Figure 4.11. Strontium isotope compositions of allochems, pre-bitumen calcite cements, and saddle dolomite. Note that all components have strontium isotopic composition similar to each other and to that of the Late Jurassic sea water.

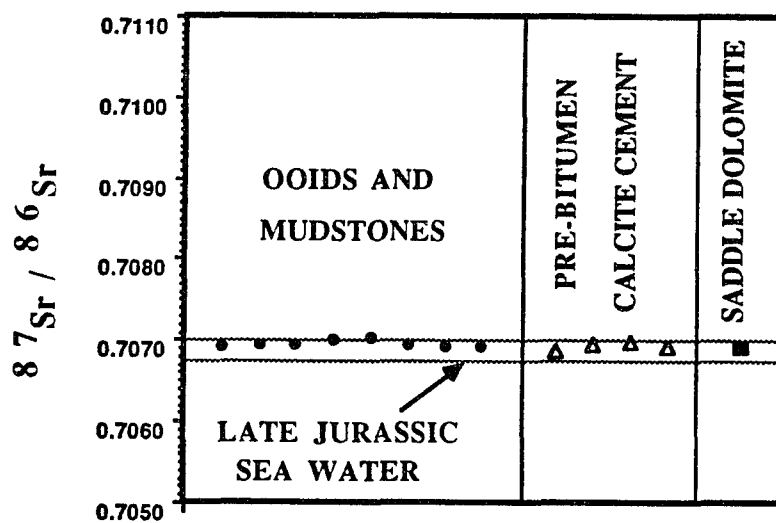


Table 4.4. Trace element (in ppm), stable oxygen and carbon isotopes (relative to PDB), and strontium isotopic composition of ooids, algally coated grains, and mudstones.

PF: Phillips #1A Flurry; PJ: Phillips #1A Josephine.

Depth (ft)	Mg	Sr	Fe	Mn	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Ooids							
PJ19219	3125	224	83	31	-3.4	2.9	
PJ19224	6009	200	129	33	-3.6	2.8	
PJ19231		217	235	37	-3.5	4.2	
PJ19241	3504	376	78	20	-3.3	2.9	
PJ19244	2985	298	21	17			
PJ19250	2933	283	78	20			
PJ19254	3542	330	32	16			
PJ19268	3453	309	56	18			
PJ19270	3956	323	38	16			
Algally Coated Grains							
PJ19270	3306	323	57	13	-3.5	3.5	
PJ19273	2337	205	45	15	-3.6	3.7	
PJ19276	3050	307	68	11	-3.4	3.5	
PJ19280	2379	198	69	15	-3.6	3.9	
PJ19289	2173	231	37	13	-3.6	3.7	

Mudstones

PJ19906	4001	365	10	13	-3.85	4.23
PJ19930	6586	263	24	23	-4.05	4.37
PJ19950	4819	898	42	20	-0.60	4.43
PJ19993	4817	505	33	49	-2.09	3.25
PJ20012	6794	363	73	54	-3.16	3.89
PF19729	2021	195	3	16	-0.61	4.26
PF19825	2412	387	23	9	-2.49	4.39
PF19826	2354	368	17	9		
PF19927	4711	468	2	15	-3.91	4.17
PF19981	3886	462	6	32	-3.05	4.05
PF20014	2249	203	9	11	-3.16	4.23

Strontium Isotopic composition of Allochems and Mudstones

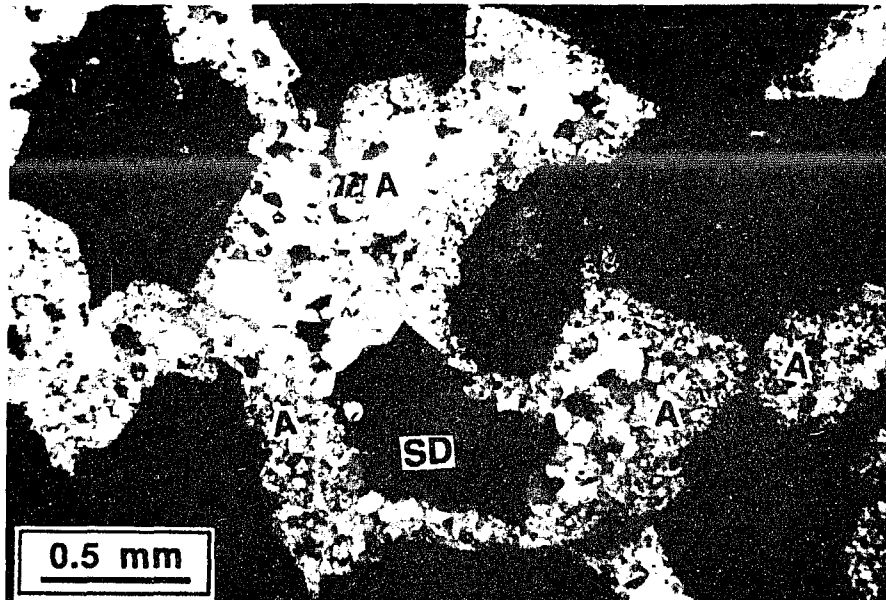
PJ19249	0.70692
PJ19283	0.70695
PJ19448	0.70696
PJ19498	0.70700
PJ19569	0.70703
PJ19876	0.70695
PJ19888	0.70694
PJ20039	0.70693

compositions range from +2.6 to +5.3 with an average of +4.5 (Table 4.3, Fig. 4.10). The bulk $\delta^{18}\text{O}$ composition of the saddle dolomite is about 3 ‰ heavier than that of the associated pre-bitumen calcite cements. This appears to be consistent with precipitation of the two minerals under equilibrium conditions (Land, 1980). One sample of saddle dolomite analyzed for radiogenic strontium has a value of 0.70693 (Table 4.3, Fig. 4.11).

Late anhydrite replaces Smackover allochems. It occurs as crystal laths and as massive replacement. The sulfur isotopic composition of the late diagenetic anhydrite (+17 CDT) is similar to the early depositional Buckner anhydrite (Chapter 1). This indicates that late diagenetic anhydrite was derived from the early Buckner anhydrite. However, secular variations sulfur isotopic composition of marine evaporites (Claypool et al., 1980) indicate that sulfur isotopic compositions of evaporites of Early and Middle Jurassic are similar to those of the Late Jurassic. Therefore, it is also possible that the late diagenetic sulfates were derived from lower Louann Formation. Most anhydrite laths in the cores sampled are calcitized. Details of this process will be given in the deep burial diagenesis of this report. However, petrographic relationships do suggest that anhydrite precipitation followed saddle dolomite formation (Fig. 4.12).

Liquid hydrocarbon migration temporarily ended

Figure 4.12. Photomicrograph (polarized light) showing calcitized anhydrite (A) which postdates saddle dolomite (SD). Phillips #1A Josephine 19,351 ft (5,902 m).



cementation in the oil containing reservoirs at Black Creek field. Similar effects in other fields have been reported by Dunnington (1967) and Koepnick (1985) for Mesozoic fields in the Middle East and Hancock and Scholle (1975) for North Sea chalks.

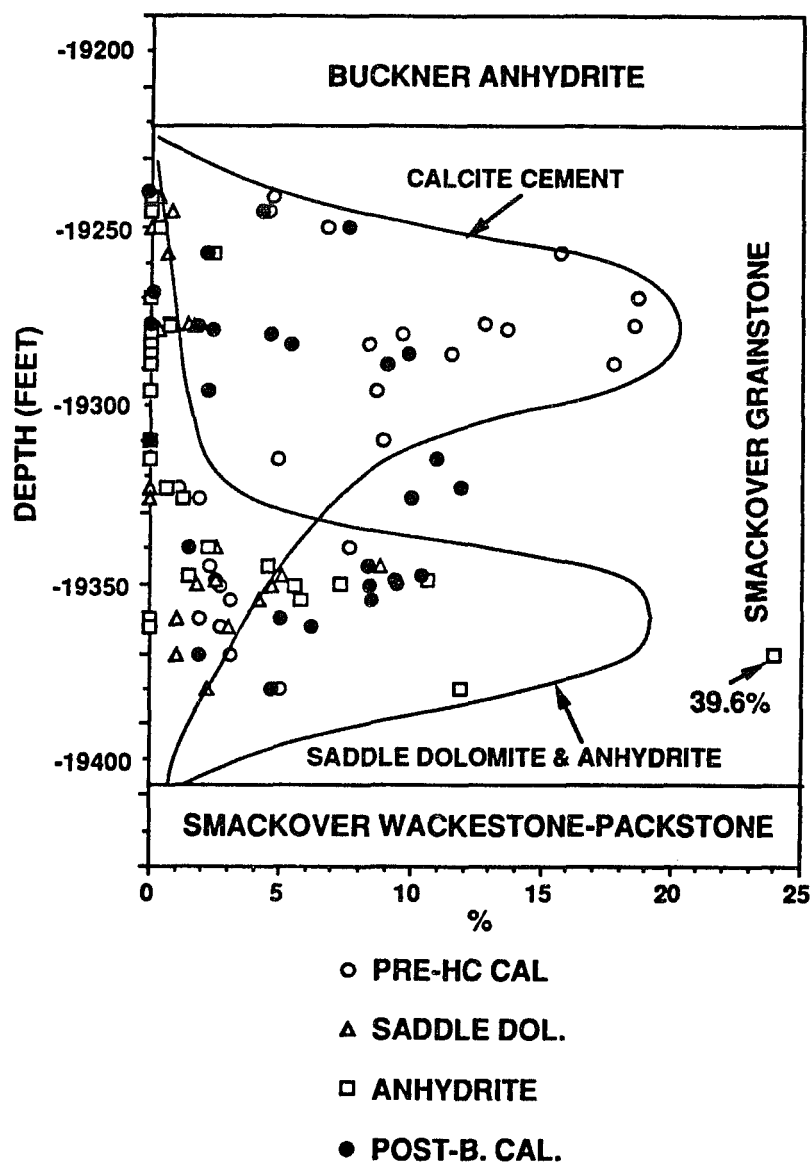
Porosity Evolution During Shallow Burial Diagenesis

Bitumen-filled pores in grainstones (Fig. 4.8) and dolomites (see below) at Black Creek field suggest that both lithofacies were porous at the time of hydrocarbon migration. The porosity types were dominantly intergranular in grainstones and intercrystalline and vuggy in dolomites. Point counting of 42 grainstone samples indicate that they have 4.7% to 18.7% pre-bitumen calcite (average= 7.8%), 0% to 8.8% saddle dolomite (average= 1.1%), 0% to 39.6% anhydrite (presently calcitized, see below, average= 2.5%), and 0% to 18.4% bitumen (average= 1.6%) (Table 4.2). This indicate that prior to precipitation of bitumen 5% to 19% of the original 45% porosity was filled by pre-bitumen calcite and saddle dolomite (Table 4.2). Since destruction of porosity is accomplished by cementation and by bulk volume reduction (Rittenhouse, 1971; Manus and Coogan, 1974; Mitra and Beard, 1981; Houseknecht, 1987), it is not clear, how much porosity was available at the time of hydrocarbon migration. However, presence of upto 18.4% bitumen-filled pore suggests that upto 18% porosity was present when

hydrocarbons migrated into the reservoir.

Pre-bitumen calcite cement, saddle dolomite and anhydrite exhibit concentration gradient in the grainstone portion of the Phillips #1A Josephine well. The pre-bitumen calcite is concentrated in the upper portion of the grainstone and saddle dolomite is more abundant in the lower part of the grainstone (Fig. 4.13). The reasons for the spacial concentration of these two pre-bitumen phases is not clear. One possibility is that the contact between the calcite and dolomite dominated portion may mark the position of paleo-oil-water contact. In this interpretation, calcite cementation was shot down by hydrocarbon migration into the upper part of the reservoir. Diagenesis, however, continued by precipitation of saddle dolomite in the lower portion of the reservoir that contained water. That means that pore waters must have been undersaturated with respect to calcite shortly after hydrocarbon migration. Data reported by Kharaka et al. (1987) indicate that Smackover pore water at West Nancy field, Clarke County (Chapter 3), where the Smackover Formation is within liquid hydrocarbon window is slightly undersaturated with respect to calcite but highly supersaturated with respect to dolomite. Calcite undersaturation was possibly caused by organic acids which are common in subsurface waters (Carothers and Kharaka, 1978; Workman and Hanor, 1985; Hanor and Workman, 1986). If similar conditions existed at Black Creek field when it was

Figure 4.13. Plot of the vertical distribution of shallow burial diagenetic phases in the grainstone portion of the Phillips #1A Josephine.



in liquid hydrocarbon window, only dolomite would have precipitated in the lower-water wet part of the reservoir.

Late diagenetic anhydrite is also more abundant in the lower portion of the grainstone but its most abundant in the lower part of the well (Appendix A, Chapter 5). The reasons for the distribution of anhydrite is not clear.

DEEP BURIAL DIAGENESIS AND POROSITY EVOLUTION

Introduction

In the Mississippi salt basin, this realm of diagenesis encompasses burial depths of 4.5 to 6 km and temperatures of 150 to 200 °C. Thermal destruction of liquid hydrocarbons, generation of large volumes of CH_4 , H_2S , and precipitation of solid bitumen (Rogers et al., 1974), created a unique diagenetic environment because post hydrocarbon migration diagenetic phases have only been observed in the deeper part of the Mississippi salt basin (Chapter 1). Further burial of the Smackover Formation after hydrocarbon migration, resulted in a more severe post-hydrocarbon migration burial history than that suffered by the sequence prior to hydrocarbon arrival into the reservoir. The post-hydrocarbon migration diagenesis was driven by high temperatures, small pore water volumes, availability of sulfates, and the presence of relatively large volumes of methane (Heydari et al., 1988). The products of this diagenesis are: (1) calcitization of anhydrite, (2) post-bitumen calcite cement,

(3) late silicification, (4) fluorite precipitation, (5) native sulfur cementation, and (6) precipitation of minor amounts of pyrite (Fig. 4.4).

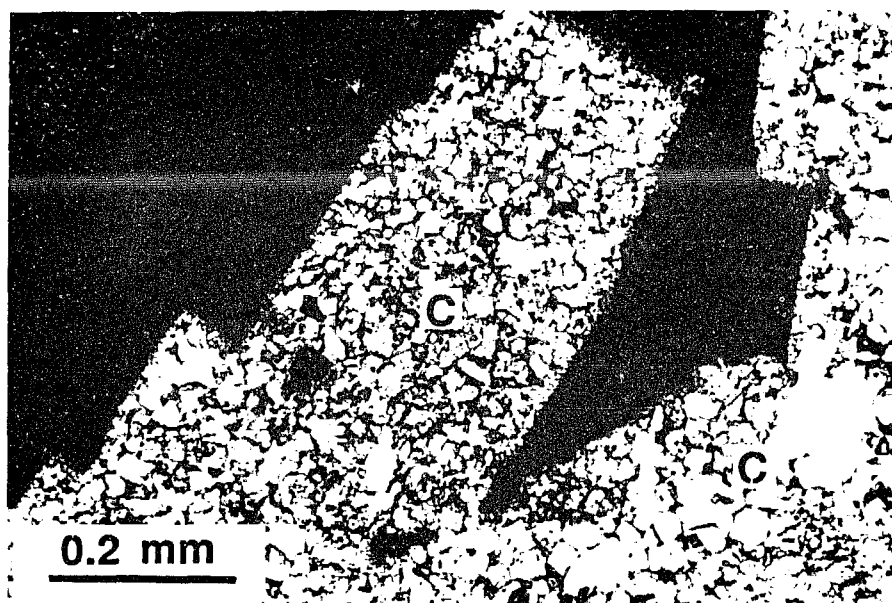
Calcitization Late Diagenetic Anhydrite

Calcitization of anhydrite can have biochemical or thermochemical origins (Orr, 1974, 1977; Trudinger et al., 1985). Anhydrite calcitization is commonly described from rocks that have experienced low temperatures, shallow burial, and fresh water flushing. In these cases, it is thought to have been mediated by the biochemical action of sulfate reducing bacteria (Davis and Kirkland, 1970, 1979; Pierre and Rouch, 1980). Calcitized anhydrite has not been observed in rocks shallower than 15,000 ft (4,575 m) in the Mississippi and the Louisiana salt basins (Badon, 1974; Moore and Druckman, 1981; Moore, 1985; Heydari and Moore, 1989). Smackover pore waters in East Nancy field (4.3 km), Clarke County, Mississippi, are undersaturated with respect to anhydrite (Kharaka et al., 1987) but no calcitized anhydrite was observed (Chapter 2, 3). Presence of calcitized anhydrite at Black Creek field with formation temperatures of over 200 °C suggest that anhydrite dissolution and calcite precipitation is of thermochemical in origin. This interpretation is supported by the similarity between sulfur isotopic composition of Late diagenetic anhydrite and elemental sulfur (Heydari and

Moore, 1989). The upper temperature tolerance of bacterial activity is not clear (Trudinger et al., 1985), but most studies indicate that it is about 80 °C (Carothers and Kharaka, 1987; Trudinger et al., 1985).

Two types of calcitized anhydrite textures, here called type one and type two, have been observed at Black Creek field. Type one is a pseudomorphic replacement of late anhydrite laths by fine (0.03 mm) equant crystals of calcite (Fig. 4.14). The replacement is thought to be of late, high temperature origin because it postdates pressure solution contacts between grains, fills late fractures, and is present only in rocks buried to depths greater than 19,000 ft (5,795 m). The replaced mineral is inferred to be anhydrite because of the presence of well developed orthorhombic crystal shapes characteristic of anhydrite (Fig. 4.14). Anhydrite inclusions are very rare in calcite crystals of type one texture. In type one texture, anhydrite was totally dissolved leaving an empty mold and calcite crystals later filled the available pore space. This is supported by the presence of bitumen as inclusion within and as pore fill between calcite crystals (Fig. 4.14). In addition calcite crystals that filled the empty mold of anhydrites continue to fill adjacent intergranular pores. This suggests that anhydrite mold and intergranular pore were parts of one pore network. Total dissolution of anhydrite suggests that diagenetic environment was high

Figure 4.14. Plain light photomicrograph showing type one calcitized anhydrite texture. Phillips #1A Flurry, 19,370 feet (5,908 m). C: calcite.

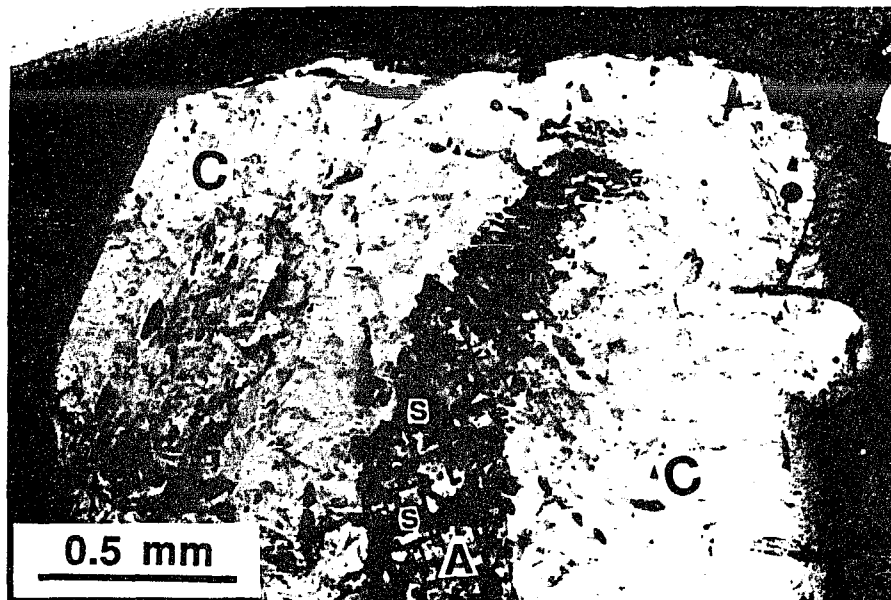


undersaturated with respect to anhydrite at this time.

In type two calcitized anhydrite texture, anhydrite nodules are replaced by mosaics of coarser calcite crystals (0.5-1.0 mm) with associated elemental sulfur (Fig. 4.15). Similar texture has also been reported by Krouse et al. (1988) from deep reservoirs in western Canada and is thought to have formed by thermochemical reduction of anhydrite.

A volume for volume replacement of anhydrite by calcite could produce secondary porosity, because the molar volumes at 25 °C and 1 bar pressure for the two minerals differ: 45.94 cm³/mole for anhydrite, versus 36.94/mole cm³ for calcite (Berner, 1971). It is commonly assumed that volume of solids is relatively independent of temperature and pressure (Helgeson et al., 1978). Molar volume of calcite, for example, calculated from the equation given by Berman (1988) is about 37.02 cm³/mole at 200 °C and 1 kilobar (conditions at Black Creek field), an increase of 0.08 cm³/mole. Berman (1988) did not provide sufficient data for volume change of anhydrite at high temperature and pressure. Therefore, the difference in molar volume among non-hydrous minerals under the reservoir temperature and pressure would be approximately the same as that under near surface conditions. Elemental sulfur produced as a result of anhydrite calcitization is commonly removed from the reaction site and would not change the volume difference between calcite and anhydrite. The absence of any secondary

Figure 4.15. Plain light photomicrograph of type two calcitized anhydrite texture. Note anhydrite inclusions (A) in calcite (C) and elemental sulfur (S) inclusions in anhydrite. Phillips #1A Flurry, 19,995 ft (6,098 m).



porosity in these fabrics suggests that the available supply of calcium carbonate to fill anhydrite molds.

The $\delta^{18}\text{O}$ compositions of type one and type two calcites that replace anhydrite are -3.9 and -3.1, respectively. The $\delta^{13}\text{C}$ of type one replacement ranges from +2.9 to +4.2 and that of type two replacement from -1.4 to -2.0 (Table 4.5, Fig. 4.16).

Post-Bitumen Calcite Cement

Regional diagenetic studies (Heydari and Moore, 1989) demonstrated that precipitation of calcite after hydrocarbon migration of bitumen precipitation is limited to the deeper portions of the Mississippi salt basin. Two types of post-hydrocarbon migration calcite cement is observed, one occurring in grainstone and the other in dolomite. Post-bitumen calcite cement in dolomite consists of very clear and large (0.5 to 10 mm.) crystals (Fig. 4.17). In some cases, pyrobitumen fills the bottom of pores and the post-bitumen calcite cement in dolomite fills the upper portion of the pore forming a "diagenetic geopetal". Four criteria conclusively demonstrate that calcite precipitated after maturation of hydrocarbons and precipitation of bitumen resulting from the thermal degradation of liquid hydrocarbons. (1) The majority of post-bitumen calcites contain inclusions of pyrobitumen (Fig. 4.17) indicating that pyrobitumen must have existed prior to calcite

Table 4.5. Trace element (in ppm), stable oxygen and carbon isotopes (relative to PDB), and strontium isotopic composition of deep burial phases. PF: Phillips #1A Flurry; PJ: Phillips #1A Josephine.

Depth (ft)	Mg	Sr	Fe	Mn	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
Calcite Replacing Anhydrite, Type I							
PJ19365					-3.8	2.9	
PJ19368					-4.0	3.4	
PJ19370					-3.9	4.2	
Calcite Replacing Anhydrite, Type II							
PF19995					-3.3	-2.0	
PF19995					-3.1	-1.8	
PF19995					-3.0	-1.4	
Post-Bitumen Calcite							
PF19892					-5.0	-15.4	
PF19892					-5.2	-10.8	
PF19904	1146	481	00	31	-5.6	-16.3	0.70705
PF19908	956	2788	00	43	-5.2	-12.2	0.70707
PF19941	1063	620	00	166	-5.0	-8.2	0.70756
PF19943	837	535	00	95	-4.7	-12.4	0.70718
PF19987	1271	935	00	36	-3.7	-1.7	
PF19987	1156	849	00	37	-3.4	-1.6	

Figure 4.16. Carbon-oxygen plot of calcites that replace anhydrite and post-bitumen calcite cement. Isotopic values for allochems, pre-bitumen calcite, and saddle dolomite are from Figure 4.12 and are shown for comparison.

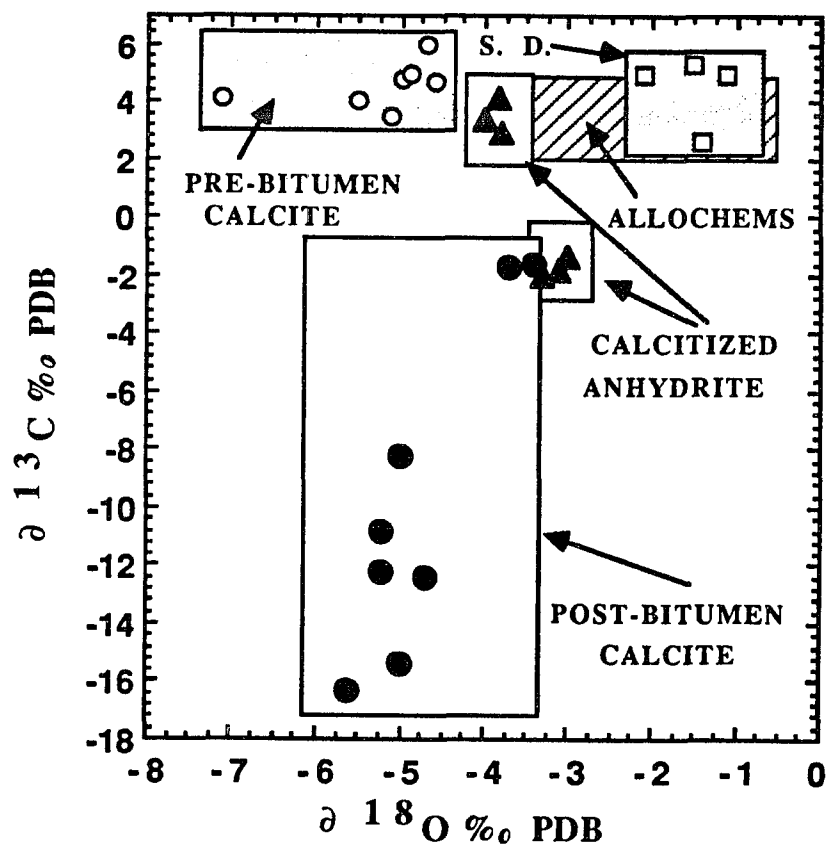
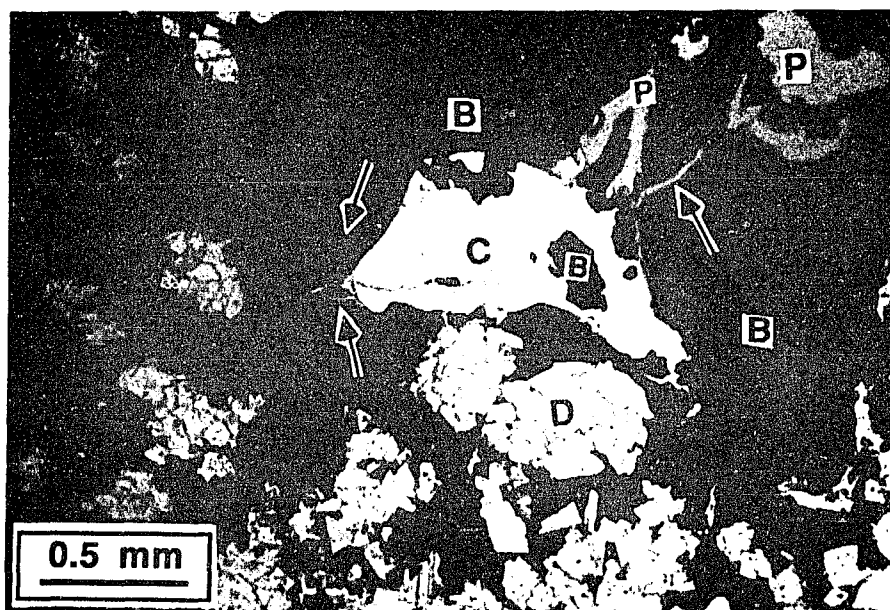
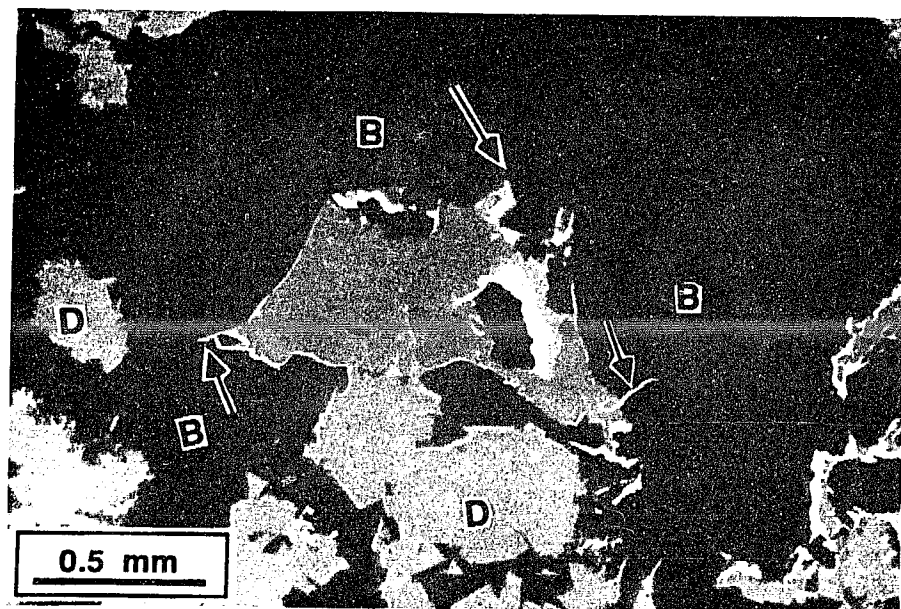


Figure 4.17. Photomicrographs showing petrographic characteristics of post-bitumen calcite. (a) Plain light, note inclusions of bitumen (B) in calcite, irregular interface between calcite and bitumen, and cracks in the pyrobitumen which are filled by calcite. These criteria indicate that calcite cement postdates bitumen formation. (b) Cathodoluminescence photomicrograph of (a). Note that luminescent zones follow irregular boundaries of bitumen. (c) Plain light, note the contacts between pyrobitumen and empty pores are as irregular as the contact between pyrobitumen and calcite. Phillips #1A Flurry, 19,894 ft (6,068 m). D: early dolomite; P: pore.

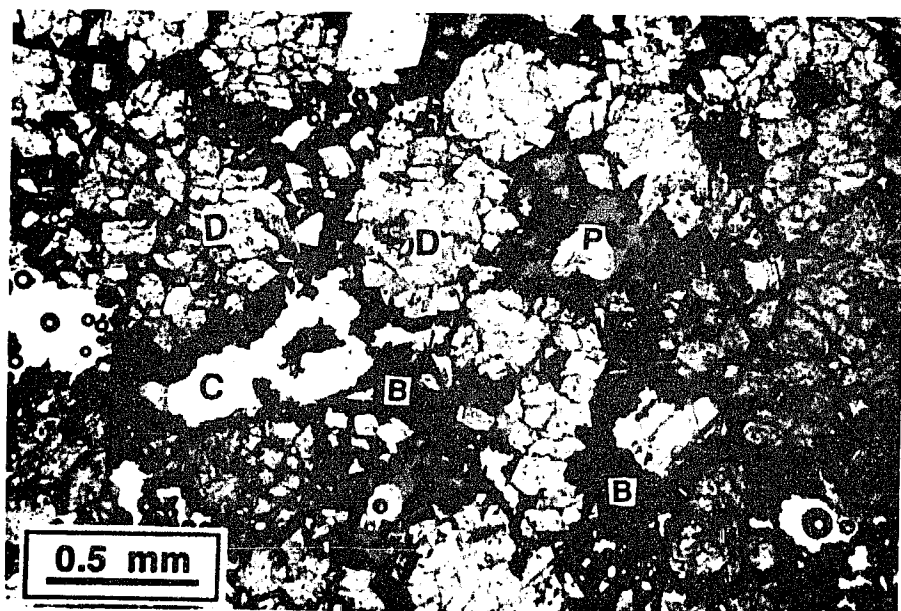


A

Figure 4.17.



B



C

cementation. None of the pre-bitumen calcites show inclusions of pyrobitumen. (2) The very irregular pyrobitumen-pore surface contact is identical to the common pyrobitumen-cement interface (Fig. 4.17A, C). This suggests that the calcite cement must have conformed to the pre-existing irregular surface of pyrobitumen. Pre-bitumen calcites exhibit straight crystal contacts with pyrobitumen (Fig. 4.8). (3) Luminescent zones of the post-bitumen calcite show that calcite crystal growth followed the pre-existing irregular surfaces of pyrobitumen (Fig. 4.17B). These irregularities must have existed prior to the growth of the calcite cement; and (4) post-bitumen calcite heals cracks formed in the pyrobitumen (Fig. 4.17A). The reason for the development of these cracks is not clear; however, it is possible that they formed during dehydrogenation of bitumen at high temperatures. Hydrogen indices of Smackover bitumens decrease with depth (Sassen, 1988), supporting this possibility.

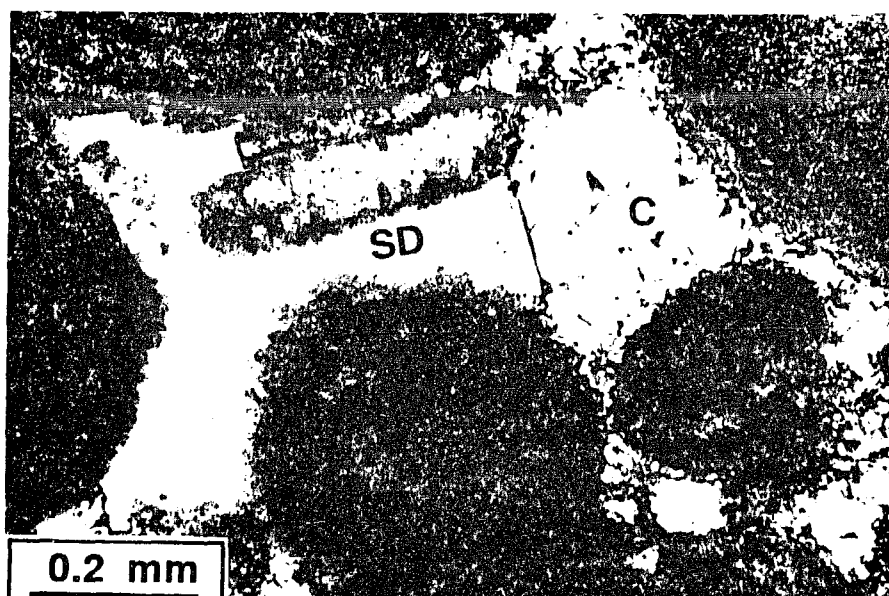
These observations demonstrate that post-bitumen calcite formed after pyrobitumen precipitation. In the Mississippi salt basin, solid bitumen is abundant as pore-fill cement in samples from wells with bottom hole temperatures of at least 120 °C in the shallower part of the basin (Heydari and Moore, 1989). This bitumen is soluble in organic solvents (e.g. methanol-chloroform). Upon increase in temperature soluble solid bitumen transforms to

pyrobitumen which is insoluble in organic solvents. Pyrobitumen is observed in wells with bottom hole temperatures of greater than 150 °C in the Mississippi salt basin. Therefore, post-pyrobitumen cement must have precipitated at a temperature of at least 150 °C.

The post-bitumen calcite cement in grainstone is a fine crystalline mosaic cement with crystals ranging in size from 0.01 to 0.2 mm (Fig. 4.18). This calcite grew from bitumen stained grains and often contains inclusions of bitumen. It clearly postdates pre-bitumen calcite cement and saddle dolomite (Fig. 4.18). It was indicated that saddle dolomite precipitated possibly because pore waters were undersaturated with respect to calcite due to presence of organic acids. Precipitation of post-bitumen calcite after saddle dolomite (Fig. 4.18) suggests that pore waters once again became supersaturated with respect to calcite. This might have occurred by destruction of organic acids due to increase in temperature. The rate of decarboxylation of organic acids is very slow at temperatures of <120 °C (Shock, 1988). This rate might have increased very rapidly when temperatures are greater than 150 °C (Carothers and Kharaka, 1978; Hanor and Workman, 1986) resulting in total destruction of organic acids.

In grainstones, the crystal size of post-bitumen calcite cement is significantly smaller than pre-bitumen calcite and saddle dolomite (Fig. 4.18). One possible

Figure 4.18. Plane light photomicrograph showing post-bitumen calcite cement (C) in grainstone postdating bitumen stained saddle dolomite (SD). Phillips #1A Josephine 19,348 ft (5,901 m).

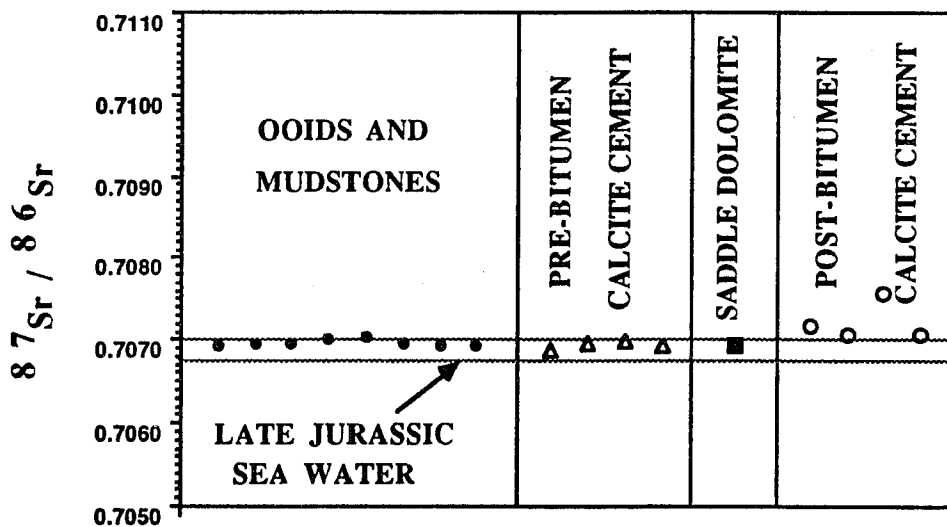


explanation is rapid rate of nucleation due to an increase in salinity of pore waters from the time of pre-bitumen cementation to the time of post-bitumen cementation. Furthermore, post-bitumen calcite cement in dolomite is significantly larger than post-bitumen calcite in grainstone (compare Figures 4.17 and 4.18). The timing of the post-bitumen calcite cements in grainstone and that occurring in dolomite relative to each another is not clear. Neither is the reason for the variations in crystal size of the post-bitumen calcite cement in grainstone and in dolomite. A slow rate of nucleation due to cementation in a dolomitic host rock might explain the difference in crystal size.

The $\delta^{18}\text{O}$ composition of the post-bitumen calcite cement in dolomites ranges from -3.3 to -5.6, with an average of -4.9. The $\delta^{13}\text{C}$ value ranges from -1.6 to -16.3, with an average of -10 (Table 4.5, Fig. 4.16). The strontium isotopic composition of the post-bitumen calcite ranges from 0.70705 to 0.70718 with an average of 0.70722 or slightly higher than pre-bitumen calcite cement (Table 4.5, Fig. 4.19). The post-bitumen calcite contains an average of 1034 ppm Sr, 1071 ppm Mg, 68 ppm Mn, and <1 ppm Fe (Table 4.5). Post-bitumen calcite dominantly exhibits dull luminescence with a single thin brightly luminescent zone (Fig. 4.17B).

Due to its small crystal size, the separation of post-bitumen calcite in grainstone was not possible. This cement is very similar to the type one calcitized anhydrite. It is

Figure 4.19. Strontium isotope compositions of post-bitumen calcite cement. Allochems, pre-bitumen calcite cements, saddle dolomite are from Figure 4.11. Note that strontium isotopic composition of post-bitumen calcite is similar to the other components.



possible that they also have similar chemistry.

Quartz Replacement

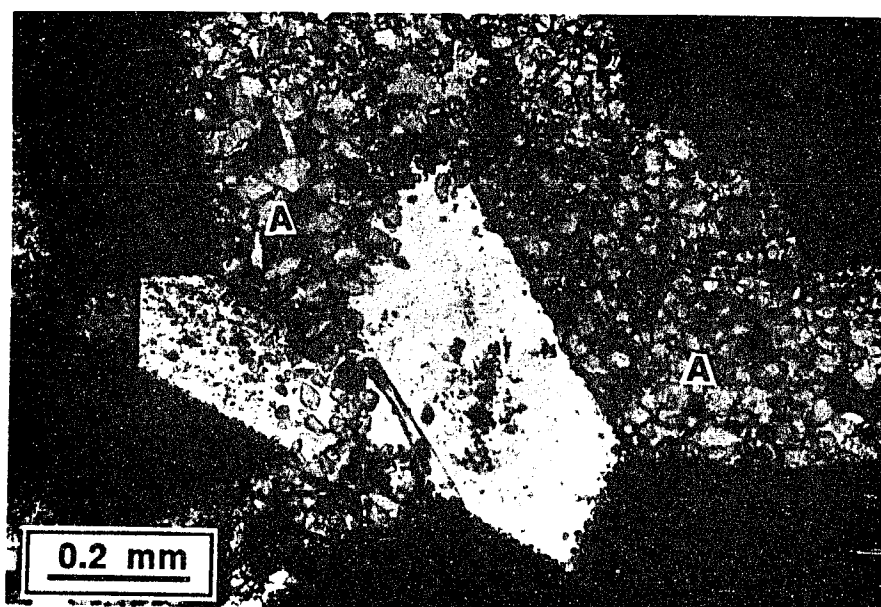
Quartz occurs most commonly as euhedral crystals replacing Smackover mudstones and packstones (Fig. 4.20A). It contains inclusions of calcites of types one and two calcitized anhydrite (Fig. 4.20B) suggesting that it partly postdated the above features. Quartz is more abundant in samples from the Josephine well. Its distribution in this well is restricted to the interval from 19,400 ft to 19,700 ft (5,917 m to 6,008 m) and above the zone where early chert nodules are concentrated (Fig. 4.2). Silica is present in only trace amounts or is absent above 19,400 ft (5,917 m). It increases to about 5 weight % at a depth of 19,600 ft (5,978 m). The silica contents of two samples from 19,630 ft (5,978 m) and 19,540 ft (5,960 m) are approximately 50 mg/cm³ of the Smackover limestone (50 kg/m³). Smackover pore waters in Clarke County, Mississippi, contain 20 mg/L Si (Kharaka et al., 1987). To supply 50 kg of silica from a water of this composition would require 2,500,000 liters of Smackover brine, assuming 100% removal of Si from pore waters. It is obvious that this volume of water is not available at the depths encountered at Black Creek field. The localized high concentration of quartz above the zone of chert nodules in the Josephine well suggests that the source for the late silica is the dissolution and remobilization of

Figure 4.20. Photomicrographs showing late silica. (A) SEM photograph of euhedral quartz replacing Smackover carbonate. Samples were etched with 1N HCl for 10 seconds, gold coated. Phillips #1A Josephine, 19,484 ft (5,943 m). (B) Late silica replacing anhydrite. Phillips #1 Josephine 19,752 ft (6,024 m).

Figure 4.20



A



B

the early cherts. This interpretation is supported by the fact that the outer layers of the chert nodules are largely replaced by calcite. Silica released as a result of this replacement may have been available for precipitation as late quartz. Quartz is soluble at pH greater than 8 even at temperature of about 100 °C (Surdam et al., 1984). The pH of subsurface waters in the Mississippi salt basin is about 5 (Kharaka et al., 1987). Dissolution of chert nodules and their replacement by calcite may suggest that silica dissolution is a surface controlled reaction. As indicated late quartz only occurs about 300 ft above the layer where chert nodules are present. This narrow range of stratigraphic distribution of late quartz may indicate that dissolved silica was transported by molecular diffusion upward and precipitated due to decrease in pH and possibly small decrease in temperature. The $\delta^{18}\text{O}$ composition of this late quartz ranges from +28.3 to +30.2 with an average of +29.5 (Table 4.6).

Fluorite

Fluorite is commonly associated with Mississippi Valley-type ore deposits. Precipitation temperatures of 100-200 °C for ore related fluorite are estimated from fluid inclusion studies (Richardson and Holland, 1979a,b; Richardson and Pickney, 1984; Spirakis and Heyl, 1988; Kesler et al., 1989). In Black Creek field, fluorite occurs

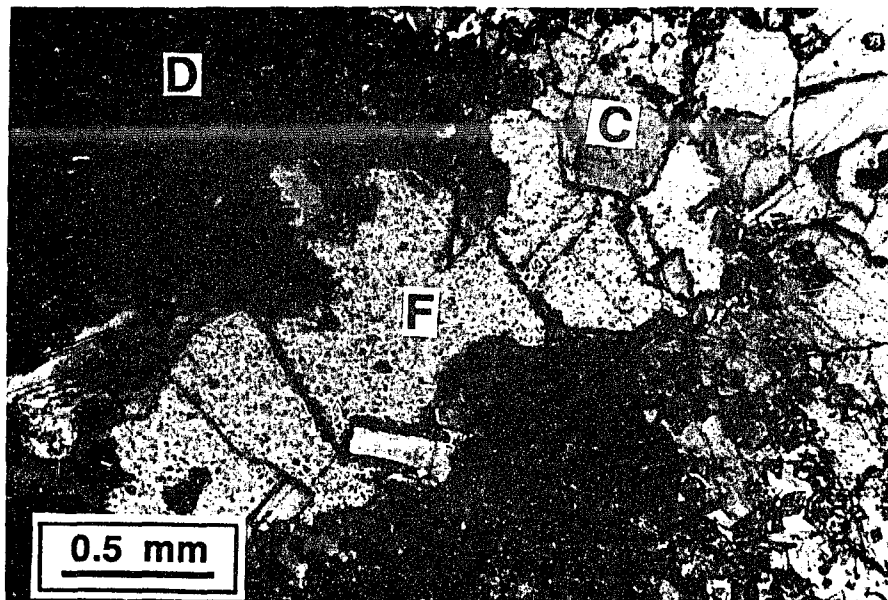
Table 4.6. Oxygen isotopic composition of the late quartz.

PJ: Phillips #1A Josephine.

Depth (ft)	$\delta^{18}\text{O}$ (SMOW)
PJ19486-1	28.3
PJ19486-2	30.2
PJ19540-1	30.4
PJ19540-2	28.8
PJ19548	28.3
PJ19570	28.9

as pore-fill cement and postdates pyrobitumen and post-bitumen calcite cement (Fig. 4.21) indicating that it is a very late phase, formed at high temperatures. It is not clear what initiated precipitation of fluorite. The Smackover pore waters contain 11 ppm F at depth of 4.3 km in Clarke County, Mississippi, (Kharaka et al., 1987). Fluorite was not observed in Smackover grainstones in that area (Chapter 3). Saturation state of Smackover pore water with respect to fluorite was not reported by Kharaka et al. (1987). Assuming that Smackover pore water in Clarke County is supersaturated with respect to fluorite, its absence may be due to formation of CaF^+ , MgF^+ , and NaF° complexes in a Na-Ca rich water. Richardson and Holland, (1979a) suggested that fluorite can precipitate either as a consequence of decrease in temperature and pressure along the flow path of hydrothermal solution or due to fluid mixing, or by interaction of solution with wall rock resulting in changes in the pH, Ca, and Mg concentration of hydrothermal fluid. There is no evidence of fluid mixing or decrease in temperature and pressure during burial of the Smackover Formation at Black Creek field. Experimental studies by Richardson and Holland (1979b) reveal that the solubility of fluorite increases with increasing temperature, ionic strength, and Ca and Mg concentration of solution. The solubility increase of fluorite with increasing Ca concentration is due to the formation of CaF^+ complex

Figure 4.21. Plane light photomicrograph showing fluorite cement (F) postdating calcite cement (C). Phillips #1A Flurry 19940 ft (6082 m).



(Richardson and Holland, 1979b). Therefore, a decrease in Ca content of the solution, calcite cementation for example, may cause fluorite precipitation. At Black Creek field, fluorite postdates post-bitumen calcite cement. It is possible that F might have been freed from CaF^+ complex as a result of the reaction of bicarbonate with CaF^+ to produce calcite cement. Similar interpretation for fluorite formation was given by Spirakis and Heyl (1988) involving reaction between MgF^+ complex and bicarbonate ions. Spirakis and Heyl (1988) indicated that bicarbonate ion has a higher affinity of Mg than F.

Pyrite

Minor amounts of pyrite were observed in samples from both wells. Pyrite occurs as very small (1-20 microns) irregular particles replacing carbonate grains and cements (Fig. 4.22). The time of pyrite formation is difficult to determine. Pyritization of some late calcite cement and late diagenetic anhydrites suggest that some pyrite formed late during burial. Although abundant H_2S was produced during post-hydrocarbon migration burial diagenesis, the absence of significant pyrite is attributed to the lack of Fe in this particular system. It should be noted that pre-bitumen calcite contains only 57 ppm Fe and post-bitumen calcite has no detectable Fe, supporting the above conclusion. The supply of Fe may be limited by the scarcity of

Figure 4.22. Backscattered SEM photomicrograph of pyrite.
Phillips #1A Josephine 19,277 (5,879 m).



siliciclastics, including the absence of the Norphlet Formation which elsewhere contains thick red beds. This is in contrast to Pine Point, Canada, where H_2S combined with metal ions brought into the mineralization site by hydrothermal fluids resulted in the precipitation of sulfide ores (Macqueen and Powell, 1983; Powell and Macqueen, 1984). In Pine Point and in Black Creek field H_2S was generated in place by thermochemical sulfate reduction. Macqueen and Powell (1983), however, suggested that sulfate reduction occurred at about 80-100 °C at Pine Point due to migration of hot hydrothermal fluids.

Elemental Sulfur

Sulfur occurs in a variety of crystalline and amorphous forms in nature (Tuller, 1954). However, the most common and most stable form at normal temperature and pressure is orthorhombic sulfur which is commonly known as S_α . This form of sulfur transforms to monoclinic sulfur or S_β at 95.5 °C. Monoclinic sulfur melts at about 119 °C at one bar pressure to form liquid sulfur upon slow heating (Fig. 4.23). In slow cooling of liquid sulfur, monoclinic sulfur forms first. This form of sulfur is unstable at normal temperature and pressure and transforms to orthorhombic sulfur with time. Liquid sulfur exhibit a unique viscosity variations with increasing temperature (Fig. 4.24). The viscosity of elemental sulfur first decreases from its melting

Figure 4.23. Graph showing different phases of elemental sulfur (Tuller, 1954). Pressure and temperatures conditions at Black Creek field plot in liquid sulfur area.

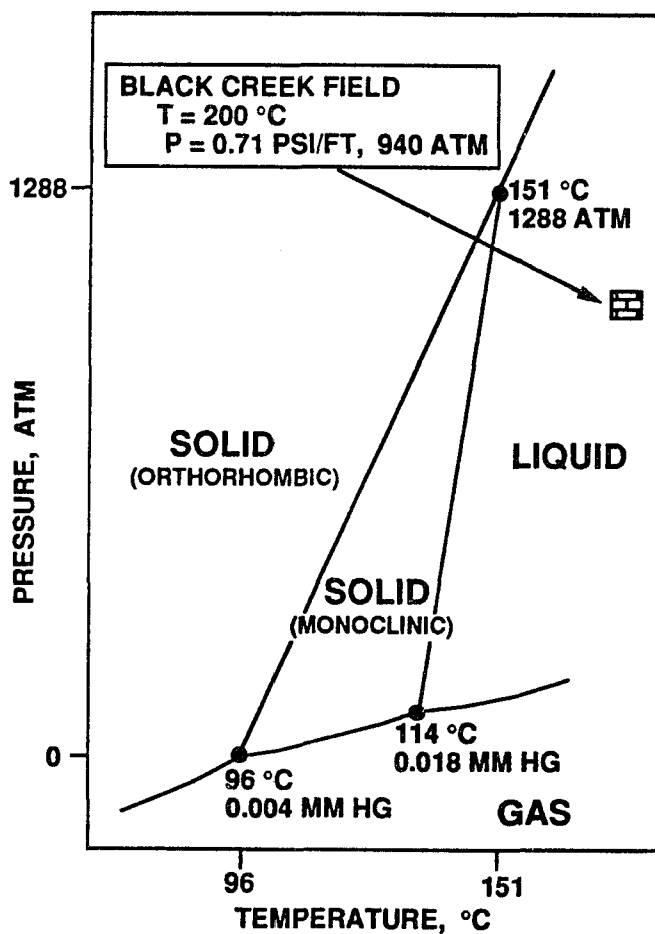
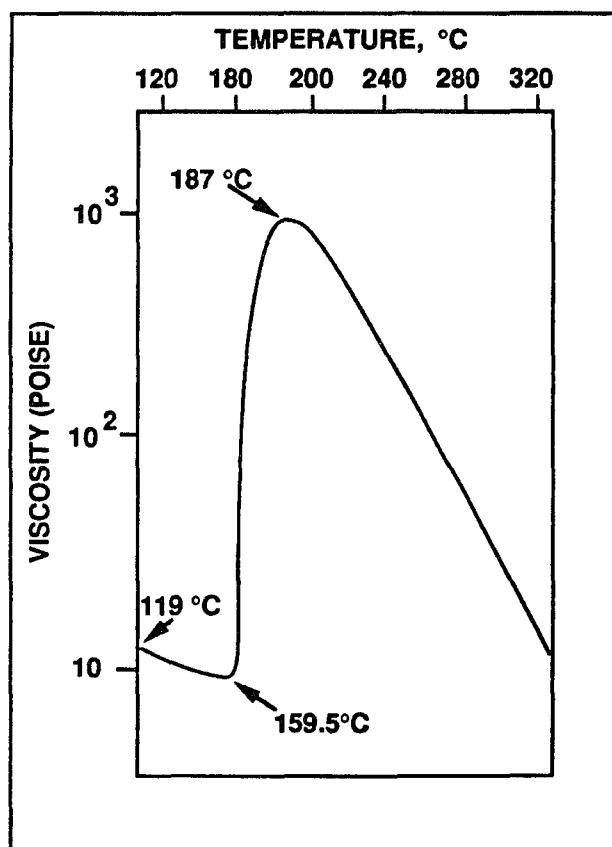


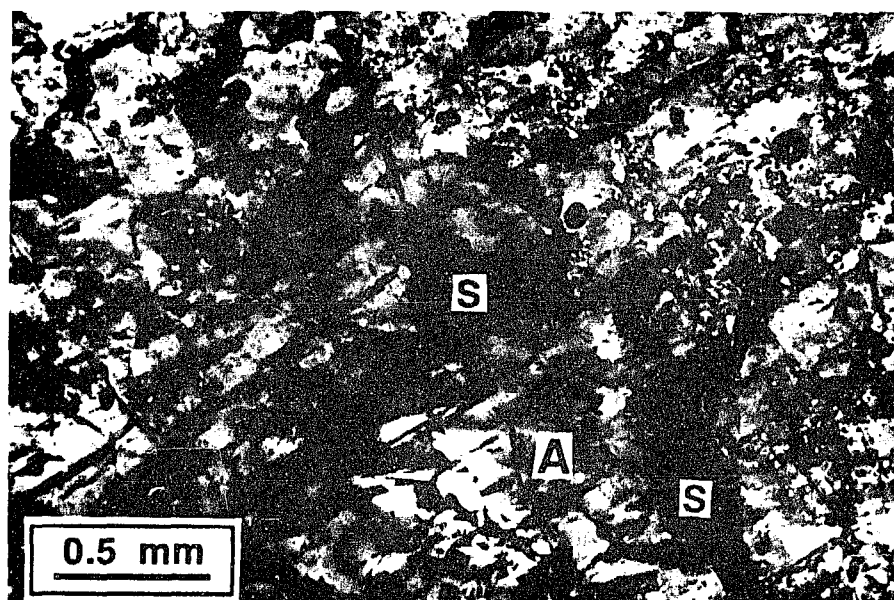
Figure 4.24. Graph showing viscosity variations of elemental sulfur with temperature at 1 atmosphere pressure (MacKnight and Tobolsky, 1965).



temperature (119 °C) to 159 °C under atmospheric pressure. It then increases very rapidly from the viscosity of about 8 poises at 159 °C to a viscosity of over 900 poises at 187 °C, and then decrease to about 10 poises at about 300 °C (Tobolsky, 1964; MacKnight and Tobolsky, 1965). The rapid increase in viscosity of liquid sulfur above 159 °C is due to breakage of S₈ sulfur rings and formation of long chain sulfur polymers (Tobolsky, 1964). Simple bubbling of H₂S into liquid sulfur at atmospheric pressure can decrease the viscosity of elemental sulfur from its maximum of 932 poises at 187 °C to less than 2 poises (Fanelli, 1949).

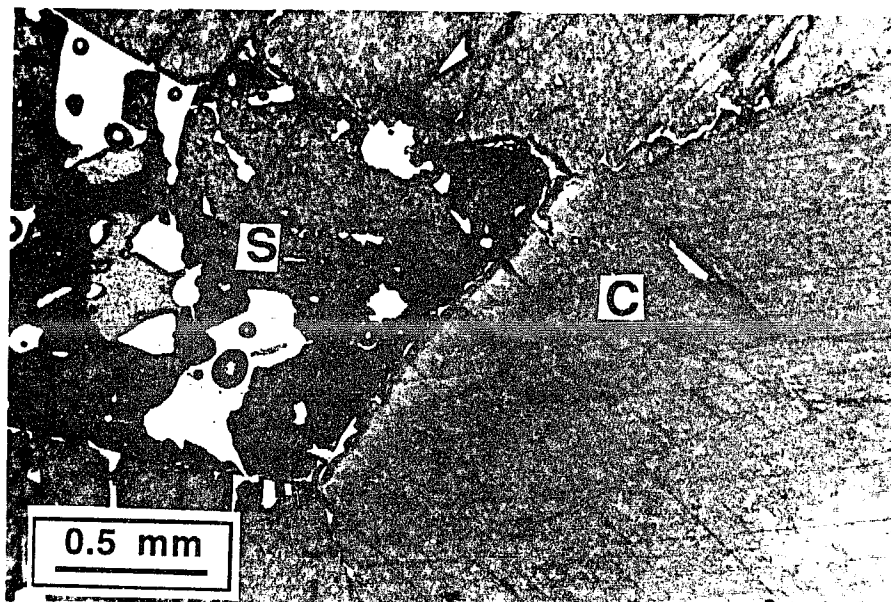
At Black Creek field, elemental sulfur commonly occurs as a replacement of anhydrite (Fig. 4.25A) and less often as pore-filling cement (Fig. 4.25B). The bottom hole temperature at Black Creek field is over 200 °C. The fluid pressure in the field is 0.71 psi/ft (Parker, 1974). Temperature and pressure conditions at this field suggest that any sulfur at reservoir temperature and pressure should exist in liquid form. When viewed with SEM, elemental sulfur is highly porous and exhibits large bubble-shaped cavities similar to pumiceous textures found in volcanic rocks (Fig. 4.20C,D). At high magnification it appears to be composed of fibers resembling curled up rope (Fig. 4.20E). These features indicate that elemental sulfur existed in a molten phase under the reservoir temperature and pressure and solidified rapidly when the cores were taken. The cavities

Figure 4.25. Photomicrographs showing characteristics of elemental sulfur. (A) Elemental sulfur (S) replacing anhydrite (A). Phillips #1A Flurry 19,995 (6098 m). (B) Elemental sulfur (S) precipitated as pore fill cement postdating calcite cement (C) (plain light and stained with alizarine red-s). Note vesicular nature of elemental sulfur. Phillips #1A Flurry, 19760 ft (6,027 m). (C,D) SEM photographs of elemental sulfur (S) formed as a result of anhydrite destruction (A). Note pumiceous texture. (E) SEM photograph of elemental sulfur composed of fibrous strings; c-e from Phillips #1A Flurry 19,995 ft (6,098 m).

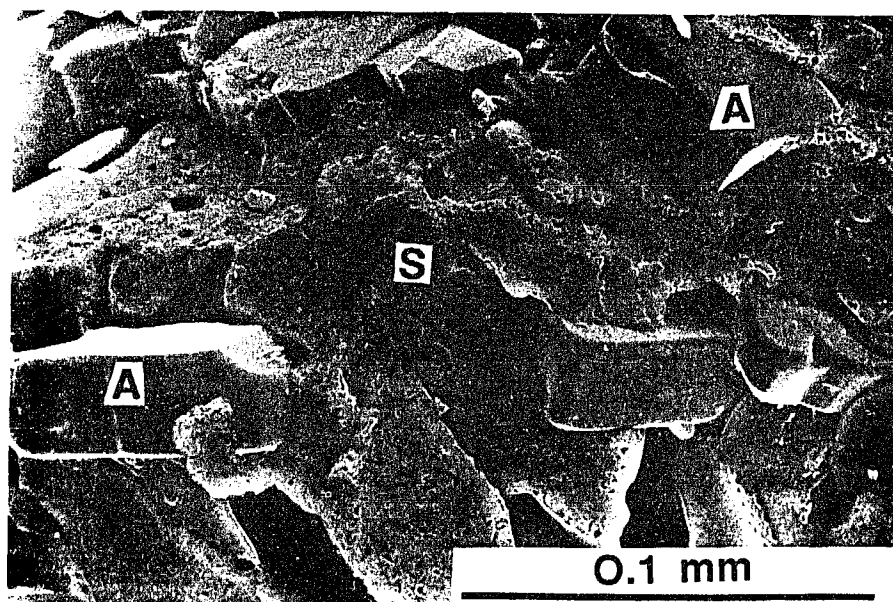


A

Figure 4.25

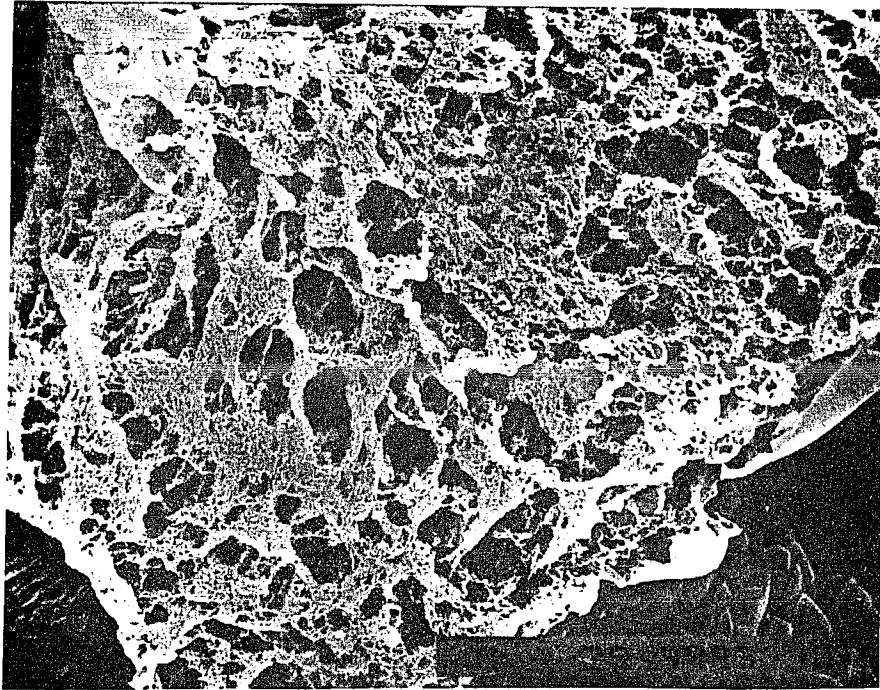


B

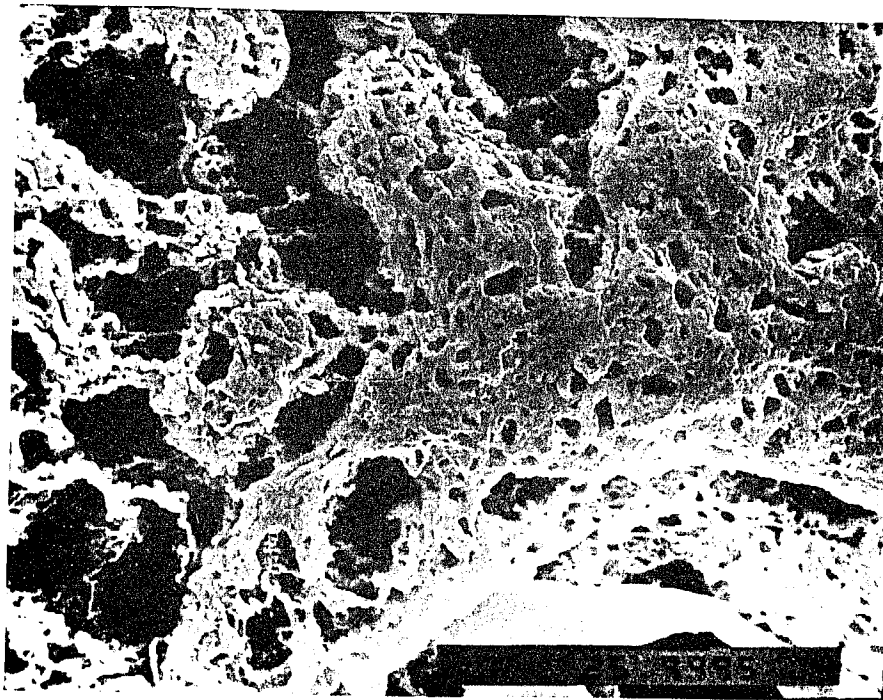


C

Figure 4.25

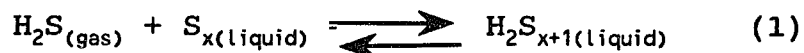


D



E

are probably produced by the escape of gases dissolved in liquid sulfur, most likely H_2S , due to release of pressure. Experimental studies indicate that H_2S gas is highly soluble in liquid sulfur and reacts with it to form hydrogen polysulfide liquid by the following reaction (Fanelli, 1949; Wiewiorowski and Touro, 1966; Hyne, 1980, 1983):



The equilibrium constant (K) for the reaction (1) is given By:

$$K = a\text{H}_2\text{S}_{x+1} / (f\text{H}_2\text{S} * a\text{S}_x) \text{ or } (f\text{H}_2\text{S} * a\text{S}_x) * K = a\text{H}_2\text{S}_{x+1} \quad (2)$$

where f =fugacity and a = activity. This relationship indicate that an increase in H_2S concentration or temperature which increase partial pressure of H_2S results in disequilibrium. For the reaction to reach equilibrium $a\text{S}_x$ must decrease. Therefore, elemental sulfur will react with excess H_2S to produce H_2S_{x+1} . In addition, Swift et al. (1976) showed that at pressures greater than 10,000 psi (690 bar) equilibrium constant for the reaction 1 (assuming $x=8$) will increase with increasing temperature and pressure. For the reaction to reach equilibrium concentration of H_2S and S should decrease. This accomplished by the formation of hydrogen polysulfide. The increase solubility of H_2S gas in liquid sulfur with increasing temperature and pressure has been shown experimentally (Fanelli, 1949; Wiewiorowski and Touro, 1966; Swift et al., 1976). Therefore, as temperature, pressures, and concentrations of H_2S decrease the reaction

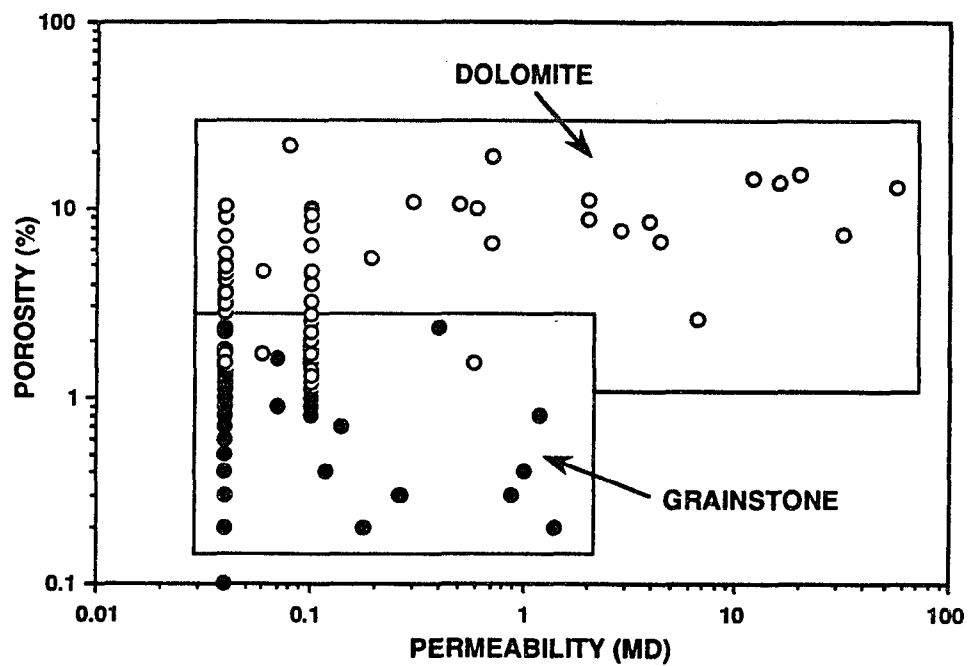
will go to the left, releasing H_2S and precipitating elemental sulfur. This is apparently the major cause of elemental sulfur precipitation in tubing in high H_2S -bearing reservoirs (Hyne, 1980, 1983) and is considered sufficient to produce the features observed at Black Creek field.

Porosity Evolution During Deep Burial Diagenesis

Core lab analyses indicate that grainstones at Black Creek field presently contain <1% porosity and <1 millidarcy permeability (Fig. 4.26). It was indicated that grainstones at this area had upto 18% porosity at the time of hydrocarbon migration and bitumen precipitation. Lack of any intergranular porosity in grainstones at the present reservoir depth suggests that pressure solution, cementation, and bitumen precipitation after hydrocarbon migration have totally destroyed the porosity in grainstones. Point counting of grainstones exhibits 0% to 18.4% bitumen (average= 1.6%) and 0% to 11.9% post-bitumen calcite cement (average= 5.0%) (Table 4.2). These two events as well as porosity decrease by bulk volume reduction are responsible for total destruction of porosity after hydrocarbon migration during deep burial diagenesis.

The dolomites on the other hand contain 1 to 20% porosity and 1-60 millidarcy permeability (Fig. 4.26). Results of point counting indicate that dolomite samples contain 2.3% to 38.8% bitumen (average= 12.8%), 0.6% to

Figure 4.26. Porosity-permeability of grainstone and dolomite samples from the Phillips #1 Flurry and Phillips #1 Josephine.



18.1% post-bitumen calcite (average= 9.3%), 0% to 2.9% fluorite (average= 0.45%), and 1.7% to 16.3% thin-section porosity (average= 6.9%) (Table 4.7). This indicates that dolomite still retains considerable porosity and permeability to form economically important hydrocarbon reservoirs under above conditions.

DISCUSSION

Oxygen Isotopes

The $\delta^{18}\text{O}$ composition of post-bitumen calcite cements in dolomite zones formed at temperatures $>150^\circ\text{C}$ ranges from -3.4 to -5.6 with an average of -4.7, while that of pre-bitumen calcite cements formed at temperatures $<100^\circ\text{C}$ ranges from -4.7 to -7.1 with an average of -5.3 (Fig. 4.16). The $\delta^{18}\text{O}$ composition of calcite which replaces anhydrite is -3.7 and is heavier than that of pre-bitumen calcite cements. The pre-hydrocarbon migration calcites show the common and well documented burial diagenetic trend of $\delta^{18}\text{O}$ depletion with increasing temperature (Fig. 4.16) (Moore, 1985; Choquette and James, 1987; Zempolich et al., 1988; Moore, 1989). However, post-hydrocarbon migration calcite cements exhibit similar or heavier $\delta^{18}\text{O}$ composition than pre-hydrocarbon migration calcite.

Rock-water interaction during shallow burial when sufficient volume of water was available (up to 50%) resulted in the depletion of $\delta^{18}\text{O}$ composition of calcite

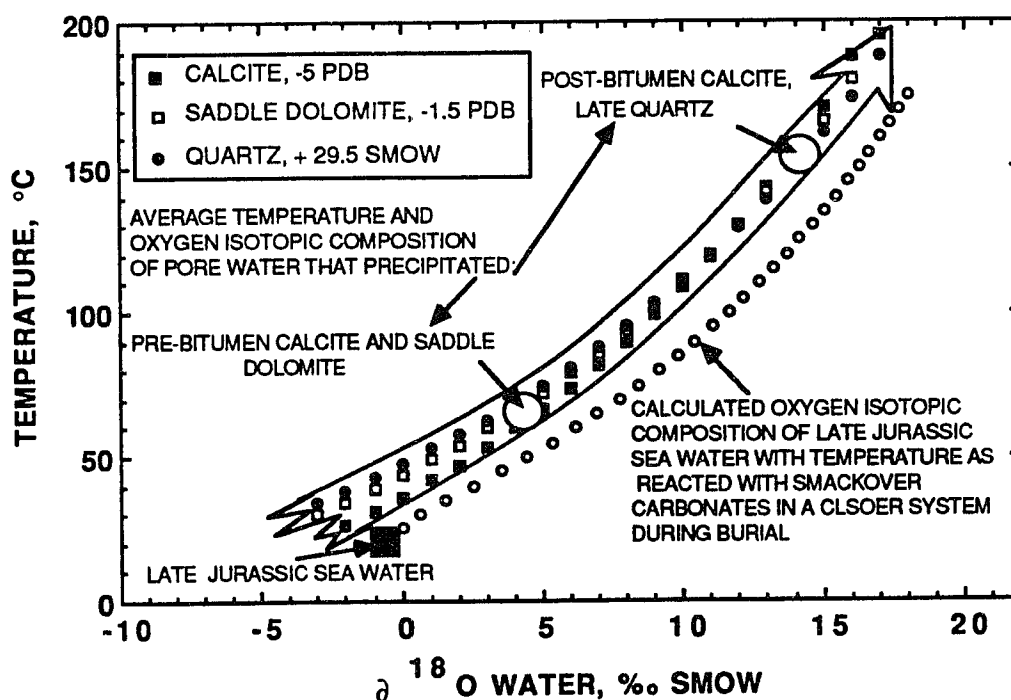
Table 4.7. Point counting data reporting concentrations of dolomite (D), bitumen (B), post-bitumen calcite cement (PBC), and porosity (P) in dolomites in Black Creek field. Sample # indicate depth of sample in feet. PF stands for Phillips #1A Flurry and PJ for Phillips #1A Josephine.

SAMPLE #	% D	% B	% PBC	% F	% P
PF19892	59.4	20.7	18.1	0.0	1.7
PF19890	81.4	4.5	13.1	0.0	1.1
PF19894	52.6	38.8	3.5	0.0	5.1
PF19903	82.1	2.3	10.8	0.0	4.8
PF19923	69.9	21.0	7.8	0.0	1.2
PF19939	66.1	10.1	13.1	1.2	9.5
PF19940	59.5	7.6	15.9	2.9	14.0
PJ19771	85.3	5.5	0.6	0.0	8.7
PJ19774	77.3	5.1	1.3	0.0	16.3
AVERAGE	70.4	12.9	9.3	0.5	6.9

cement. At Black Creek field, for example, the $\delta^{18}\text{O}$ values of pre-bitumen calcite cements ranges from -4.7 to -7.1 (Table 4.3, Fig. 4.16). The depletion trend in calcite cement is the result of carbonate-water temperature fractionation in cases where sufficient water is available (O'Neil et al., 1969). The depletion trend in calcite cement will be accompanied by a simultaneous increase in $\delta^{18}\text{O}$ composition of remaining pore waters. Under deeper burial conditions, and after hydrocarbon migration, pore water volume decreases significantly (<10%) due to porosity occlusion. In this case, which acts essentially as a closed system, the $\delta^{18}\text{O}$ composition of pore water tend to become significantly heavier not only due to temperature fractionation between carbonate minerals and water but also due to buffering of the water by the host carbonate rocks. Therefore, a pore water with high $\delta^{18}\text{O}$ composition can precipitate a calcite with relatively heavy $\delta^{18}\text{O}$ value at high temperatures. The post-bitumen calcite cements at Black Creek field seemed to have formed under these conditions. Therefore, the $\delta^{18}\text{O}$ composition of calcite cements field suggests that late burial diagenesis of the Smackover in this field took place in a progressively more closed system.

The equilibrium precipitation line of saddle dolomite with a $\delta^{18}\text{O}$ composition of -1.5 and that of late quartz with $\delta^{18}\text{O}$ of +29.5 plot very close to that of the post-bitumen calcite cements (Fig. 4.27). In this pore water evolution,

Figure 4.27. Postulated oxygen isotopic evolution of the Smackover pore waters in Black Creek Field. Equation for calcite-water, $1000 \ln \alpha = 2.78 \times 10^6 \times T^{-2} - 3.39$ (O'Neil et al., 1969) and dolomite-water, $1000 \ln \alpha = 3.14 \times 10^6 \times T^{-2} - 2.0$ (Land, 1983), quartz-water $1000 \ln \alpha = 3.38 \times 10^6 \times T^{-2} - 3.40$ (Clayton et al., 1972). Oxygen isotopic composition of Late Jurassic sea water is derived from the oxygen isotope composition of belemnites (Tan and Hudson, 1974, Fisher, and Arthur, 1977).



it may be seen that pre-bitumen calcite and saddle dolomite precipitated at an average temperature of 60 °C from a pore water with $\delta^{18}\text{O}$ of +3 to +4 (Fig. 4.27). Late silica and post-bitumen calcite formed at about 150 °C from a pore water with a $\delta^{18}\text{O}$ composition near +15 (Fig. 4.27).

Figure 4.27 also shows the result of modeling of variations of $\delta^{18}\text{O}$ of a pore water with depth in a closed system using the following the mass balance equation of Taylor (1977):

$$W (\delta_h^f - \delta_h^i) = R (\delta_c^i - \delta_c^f) \quad (3)$$

where i=initial composition; c= mineral-in this case calcite; f= final composition; h= water; W= atomic % oxygen in water; R= atomic % oxygen in rock; W and R are calculated from porosity-depth equation by Schmoker and Halley (1982):

$$P = 41.73 e^{-z/2498} \quad (4)$$

where z= depth in meters; P= porosity.

δ_m^f is calculated from the calcite-water fractionation equation of O'Neil et al, (1969):

$$\delta_c^f = (2.78 \times 10^6 T^{-2} - 3.39) + \delta_h^f \quad (5)$$

The assumptions are: (1) an initial pore water with a $\delta^{18}\text{O}$ of 0 ‰ SMOW (sea water); (2) an original rock with $\delta^{18}\text{O}$ of -2 ‰ PDB (Smackover carbonates); and (3) a geothermal gradient of 25 °C/km. Successive changes in the composition of the pore water were calculated for 200 m intervals as a function of temperature and shown (Fig. 4.27). The trend of the calculated $\delta^{18}\text{O}$ of water with temperature closely

parallels the one derived from mineral equilibria. The above pore water evolution is similar to the oxygen isotope enrichment trend with depth of the pore waters in most sedimentary basins (Clayton et al., 1966; Sheppard, 1986). However, waters with a $\delta^{18}\text{O}$ composition as heavy as those proposed for Black Creek field have only been reported from the Cretaceous of south Texas by Land and Prezbindowski (1981).

The above pore water evolution trend occurs when sediments are continuously buried in a relatively closed system. Similar conditions seem to have existed for the siliciclastic deposits in the Texas coastal plain. The $\delta^{18}\text{O}$ evolution of their pore water (derived from silicate-water equilibria) reported by Yeh and Savin (1977) shows a trend with depth similar to the one presented in this study. By contrast, during open system diagenesis, when significant volumes of meteoric water can pass through rocks, cements with highly variable $\delta^{18}\text{O}$ values will form and a more complex pore water evolution will result. Such systems are described from the western Canada sedimentary basin by Aulsted et al. (1988) and Ayalon and Longstaffe (1988).

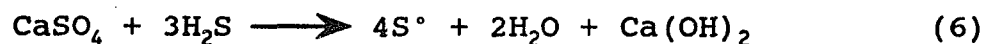
Carbon Isotopes

The $\delta^{13}\text{C}$ values of pre-bitumen calcite cements (+4) are positive and exhibit little variation (Table 4.3, Fig. 4.16). This isotopic pattern suggests that the carbon

composition of the pore waters during shallow burial diagenesis was totally buffered by the host carbonate rocks.

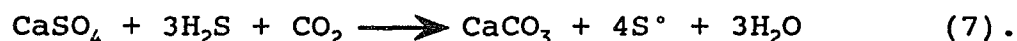
The $\delta^{13}\text{C}$ of calcite in type one calcitized anhydrite ranges from +2.9 to +4.2 and that of calcite in type two calcitized anhydrite from -1.4 to -2.0 (Table 4.3, Fig. 4.16). Calcites formed by low temperature bacterial reduction of sulfates typically exhibit a much lower $\delta^{13}\text{C}$ composition, ranging from -5 to -40 (Davis and Kirkland, 1970, 1979; Sassen, 1980; Hovland et al., 1988; Pierre and Rouch, 1988). The low $\delta^{13}\text{C}$ values of these calcite are derived from organic compounds involved in the bacterial sulfate reduction. It was expected that the calcites that replace anhydrite and formed by thermochemical reduction sulfates at Black Creek should also have a light $\delta^{13}\text{C}$ composition; since $\delta^{13}\text{C}$ composition of the Smackover oil ranges from -22 to -26 and that of methane from -38 to -45 (Sassen and Moore 1988; Claypool and Mancini, 1989). The relatively heavy $\delta^{13}\text{C}$ compositions of calcites that replace anhydrite reported in this study can be explained as follow. It was indicated that calcite type one calcitized anhydrite precipitated after total dissolution of anhydrite, generation of an anhydrite mold, and precipitation of calcite cement in the mold, actually a cementation event and not a true replacement. The exact process for total dissolution of anhydrite is not clear because the reaction products were removed from the reaction site. Anhydrite

dissolution might have taken place by the reaction (6):



The $\delta^{13}\text{C}$ composition of the calcite that filled the molds of anhydrite (+2.9 to +4.3) suggest that the main source of carbon for calcite in type one calcitized anhydrite was derived from the host carbonate rocks, most likely by pressure solution.

Type two calcitized anhydrite seemed to have formed by replacement of anhydrite by calcite through a reaction front very similar to aragonite to calcite transformation. The $\delta^{13}\text{C}$ value of this calcite (-1 to -2) indicates a minor contribution from organic carbon. It is suggested that the calcite in type two calcitized anhydrite formed by the following reaction (Siebert, 1985):

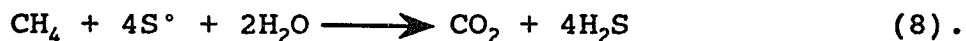


The CO_2 in reaction 7 might have had multiple sources. It is suggested that subsurface CO_2 is generated by thermal breakdown of limestone and dolomite (Farmer, 1965). Carbon isotopic composition of CO_2 gas in subsurface waters indicates dissolution of carbonate rocks in the basin (Krouse, 1980). Finally, thermochemical destruction of hydrocarbons (Orr, 1974, 1977) and decarboxylation of organic acids also produces CO_2 (Carothers and Kharaka, 1978; Hanor and Workman, 1986; Shock, 1988). The $\delta^{13}\text{C}$ composition of calcite in type two calcitized anhydrite indicate that the CO_2 used in reaction 7 was most likely

derived from thermal break down of organic compounds but was equilibrated with carbonate derived from the pressure dissolution of the host carbonate rock.

The interpretation for sulfate reduction (reactions 6 and 7) supports experimental studies (Toland, 1960; Drean, 1978; Orr, 1982) in which sulfates did not react with organic compounds even at temperatures of over 300 °C when H₂S was not present. The elemental sulfur product in the above reactions is rapidly removed from the reaction site either by reaction with hydrocarbon gases to produce more H₂S or by reaction with remaining H₂S gas to produce hydrogen polysulfide liquid as shown by equation 1, or it can simply flow away.

The $\delta^{13}\text{C}$ composition of post-bitumen calcite (-2 to -17) indicates some contribution of carbon from hydrocarbon gases. It seems that the light carbon may have been derived by the reaction of reservoir methane with elemental sulfur as shown in reaction 8 below:



Elemental sulfur is a very strong dehydrogenating agent. It has been shown that liquid sulfur reacts with methane and other alkanes to produce H₂S and CO₂ (Pryor, 1962; Voronkov, et al., 1987).

Strontium Isotopes

The strontium isotopic composition of allochems, pre-

bitumen calcite, saddle dolomite, and post-bitumen calcite in dolomite are similar to one another and to the values for the Late Jurassic sea water (0.7070) (Burke et al., 1982) (Fig. 4.19). This is in contrast to the elevated strontium isotopic composition of shallow burial cements and saddle dolomites reported from elsewhere in the Smackover (Moore, 1985). The elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these calcites and dolomites reflects the influence of basinal fluids that had interacted with feldspar and clay-bearing clastics (Moore, 1985). Since the Black Creek diagenetic components have a Jurassic seawater strontium isotopic composition, one must conclude that the pore fluids responsible for these cements have not seen significant siliciclastic sequences and have been totally buffered instead by Jurassic limestones and Jurassic seawater. Several factors may have been responsible. First, the siliciclastic Norphlet directly underlying the Smackover is not present at Black Creek field (Fig. 4.2). In addition, the reservoirs at this field may well be isolated from adjacent siliciclastics by fine grained limestones resulting a closed diagenetic system. Elsewhere, where burial cements show elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the Smackover carbonates were often underlain by feldspar and clay rich siliciclastic sequence of the Norphlet Formation and were a part of a wide spread hydrologic system (Moore, 1985).

Trace Elements

In contrast to stable and radiogenic isotopes, utilization of trace element compositions of carbonate cements as diagenetic tracers is quite difficult in most cases. This is due to the uncertainty regarding distribution coefficients of trace elements incorporated in calcite and dolomite. The coefficients are not only ill-defined at elevated temperatures and pressures but also vary with temperature, salinity, and precipitation rate (Lorens, 1978; Pingitore and Eastman, 1986). For example, distribution coefficient of Sr incorporation in calcite increases with increasing temperature based on the experiments of Kinsman (1969), is relatively constant based on data from Katz et al. (1972), and increases according to Stoessell et al. (1987). Therefore, the conclusions derived from the trace element studies are qualitative at best. The trace element compositions of cements are discussed first and then those of allochems.

Cements

The low Sr concentration of the pre-bitumen calcite (103 ppm) suggests that either the pore waters that precipitated this cement had low Sr/Ca ratio than as the present day Smackover brine in East Nancy field, Clarke County Mississippi (Chapter 3) or the distribution coefficient used are too high. The molar ratio Sr/Ca ratio

of Smackover pore water in East Nancy field is about 0.0182 (data from Kharaka et al., 1987). A calcite precipitated from the Smackover brine in East Nancy field at 100 °C should have approximately 1273 ppm Sr if we use distribution coefficient of Kinsman (1969) or 430 ppm Sr if we use that of Stoessell et al. (1987) respectively. Both values are significantly higher than Sr content of the pre-bitumen calcite cement in Black Creek field (100 ppm). Furthermore, slow rates of precipitation (typical of burial cements) must have significantly reduced the distribution coefficient of Sr (Lorenson, 1978; Moore, 1985) and, therefore, Sr incorporation into this calcite.

Low Mg concentration of these calcites (2879 ppm) indicates that they may have precipitated from a water with low Mg/Ca ratio, which is characteristic of subsurface pore waters (Carpenter et al., 1974; Hanor, 1979; Land and Prezbindowski, 1981; Stoessell and Moore, 1985). Low concentrations of Fe and Mn in the pre-bitumen calcite cements (60 and 57 ppm, respectively) suggest very low Fe/Ca and Mn/Ca ratios in water that precipitated these cements.

The high Sr concentration of post-bitumen calcite (1034 ppm) suggests its precipitation from a Sr-rich water. Because this calcite precipitated after bitumen emplacement, it may be possible to relate its trace element composition to a brine similar to that of the present day Smackover brines in East Nancy field (Chapter 3). The Smackover brine

in this field has a Sr/Ca ratio of about 0.0182 at a depth of about 4.5 km (data from Kharaka et al., 1987). Using this Sr/Ca ratio and a distribution coefficient of 0.04 at 150 °C (extrapolated from Kinsman, 1969) or 0.048 (for calcite precipitated from a Na-Ca-Cl brine at 150 °C reported by Stoessell et al., 1987), results in a calcite with Sr concentration of about 700 ppm. This is sufficiently close to the measured Sr concentration of the post-bitumen calcite to suggest that it precipitated at high temperature from a solution similar to present day Smackover brine at East Nancy field.

Low Mg concentrations of the post-bitumen calcite (1072 ppm) suggests precipitation of this calcite from a pore water with low Mg/Ca ratio. Most distribution coefficient for Mg are derived by experiments at 25 °C (see Mucci and Morse, 1981). Experiments at elevated temperatures have involved mineral replacement rather than cementation (Katz, 1973). For the purpose of this study, a distribution coefficient of 0.11 at 150 °C was extrapolated from the data of Fuchtbauer and Hardie (1975) and the Mg/Ca ratio of the Smackover brine in East Nancy field (about 0.162). It can be calculated that a cement precipitated under these constraints should contain approximately 4320 ppm Mg. This is about four times the measured Mg of post-bitumen calcite. The discrepancy suggests that pore waters at Black Creek field had lower Mg/Ca than the present Smackover brine in

East Nancy field or else the distribution coefficient extrapolated for this study is too high.

The post-bitumen calcite cement has no detectable Fe suggesting lack of Fe in the pore water. The Fe content of Smackover brines varies from 0 to over 200 ppm (Carpenter et al., 1974; Kharaka et al., 1987). The Fe concentration of the pre-bitumen cements is very low (57 ppm) indicating low Fe concentrations in the pore waters prior to the precipitation of post-bitumen calcite. Available Fe was very likely stabilized as pyrite under high H_2S conditions prior to precipitation of post-bitumen calcite in Black Creek field. This resulted in a Fe-deficient pore water that precipitated Fe-free post-bitumen calcite.

The Mn concentration of the post-bitumen calcite varies from 31 to 166 ppm. The distribution coefficient of Mn in calcite is not well known, however it is apparently greater than 1 (Pingitore, 1978). The low but measurable Mn concentration of the post-bitumen calcite suggests that the reducing conditions at Black Creek field which stabilized and removed Fe from the pore fluids did not affect Mn.

Ooids and Micrites

Table 4.3 shows the trace element compositions of ooids, algally coated grains, and micrites at Black Creek field. Ooids contain 3688 ppm Mg, 284 ppm Sr, 83 ppm Fe, and 23 ppm Mn. Micrites contain 4059 ppm Mg, 407 Sr, 22 ppm Fe,

and 23 ppm Mn. Preservation of microstructural details as well as low Sr composition suggest that ooids, algally coated grains, and micrites were originally composed of calcite containing an unknown amount of Mg. Modern marine high Mg-calcite ooids contain 10-18 mole% Mg and about 2000 ppm Sr (Land et al., 1979; Brand and Veizer, 1983; Veizer, 1983). Assuming that these components had a trace element composition similar to the present high-Mg calcite grains, they must have lost a major portion of their Mg and Sr during burial. All other diagenetic evidence presented above indicates that a depletion of Mg and Sr to the level presently observed could not have taken place by recrystallization with meteoric pore water as it is suggested for other sequences (Kinsman, 1969; Pingitore, 1976, 1978; Morrow and Meyers, 1978; Brand and Veizer, 1980). Trace element composition of deep sea chalks (Matter et al., 1975; Baker et al., 1981) suggest that stabilization in marine water will also result in significant depletion in Sr of these sediment. It was demonstrated by Land (1979) that chalk stabilized in meteoric waters show similar Sr depletion trend to those stabilized in marine water. Therefore, Sr and Mg depletion of the Smackover allochems and micrites may have occurred in marine water. This conclusions is further supported by the fact that Smackover micrites precipitated in deep water environments have similar Mg and Sr composition to the Smackover ooids formed

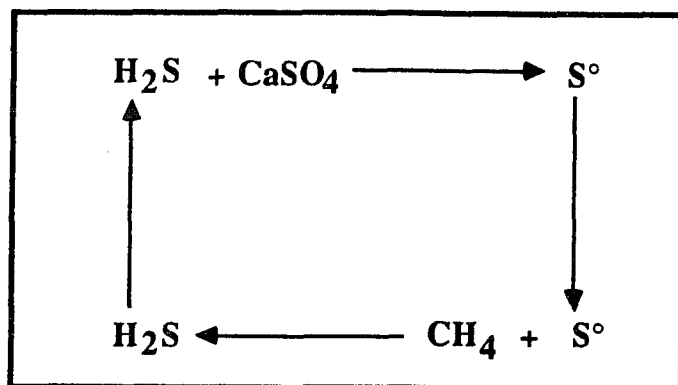
in shallow water conditions. In addition, very low Fe and Mn concentrations of ooids (83 and 23 ppm, respectively) and micrites (13 and 23 ppm, respectively) supports this interpretation.

SIGNIFICANCE OF BLACK CREEK FIELD FOR HYDROCARBON PRESERVATION AND DESTRUCTION

Vitrinite reflectance values calculated from the burial history curve (time-temperature) on top of the Smackover Formation (Fig. 4.3) indicate that the Smackover reservoir is within the dry gas window. Theoretically then, there should still be a significant volume of methane present in the reservoir. However, the gases in this field are composed of 78% H₂S, 20% CO₂, and 2% CH₄ (Grizzaffi and Thompson, 1970; Parker, 1978). The fact that methane is stable to temperatures of 400 °C (Takach et al., 1987) suggests that it must have been destroyed by processes other than high temperatures and deep burial. The Norphlet Formation at similar depths in Mobile Bay, Alabama, produces significant amount of hydrocarbons (Dixon et al., 1989). The virtually complete destruction of hydrocarbon gases at Black Creek field was the result of the specific diagenetic conditions at this field and can be explained as follows. First, thermal degradation of organic sulfur in liquid hydrocarbons produced some H₂S, which at higher temperatures reacted with the reservoir sulfates to produce elemental sulfur (reaction

6 and 7). This reaction is exothermic (Orr, 1974, 1977) raising reservoir temperature which in turn increases the rate of reaction if heat transport is not efficient. Next, elemental sulfur reacted with hydrocarbon gases to produce more H_2S (reaction 8) which reacted with anhydrite to produce more elemental sulfur in a self reinforcing cycle (Fig. 4.28). There are three ways to stop the cycle: (1) removal of H_2S by reaction with metal ions to produce metal sulfides; (2) depletion of reactant sulfate; and (3) depletion of reactant hydrocarbon gases. The first two factors may be responsible for preservation of hydrocarbons in the Norphlet Formation in Mobile Bay because this formation contains abundant Fe and limited sulfate. In addition, a recent study by Wade et al. (1989) suggests that the concentration of H_2S in reservoirs of the eastern Smackover trend is a function of the steady state flux of H_2S from Smackover reservoirs to underlying Norphlet siliciclastics. This flux is generally controlled by the thickness and porosity of the lower member of the Smackover and requires the presence of a sulfide sink (the Norphlet Formation) to react with H_2S . Consistent with these observations, the following factors are sufficient to have eliminated virtually all hydrocarbons at Black Creek field: (1) a closed system of diagenesis in which H_2S could not physically escape. This resulted in an increase in the rate of thermochemical sulfate reduction (Orr, 1982); (2) the

Figure 4.28. Simplified sketch showing sulfate- H_2S - S° -methane reaction cycle.



absence of the Norphlet Formation to serve as a sink for H_2S even if H_2S could migrate out; (3) insufficient Fe or other metal ions within the system to stabilize H_2S in place; and (4) abundant supply of anhydrite.

CONCLUSIONS

The diagenetic history of the Smackover Formation at Black Creek field is characterized by the following:

(1) Early diagenesis was dominated by marine cementation, dolomitization, and chertification.

(2) Shallow burial diagenesis is characterized by precipitation of pre-bitumen calcite, saddle dolomite, and anhydrite. All cementation events occurred late, after significant burial, and formed at temperatures of less than 100 °C. The $CaCO_3$ for the calcite and dolomite cements came dominantly from pressure solution and stylolitization. Hydrocarbon migration temporarily ended cementation.

(3) Deep burial diagenetic events include calcitization of anhydrite, precipitation of post-bitumen calcite cement, silicification, fluorite cementation, and elemental sulfur cementation. These phases precipitated under deep burial conditions at temperatures greater than 150 °C.

(4) The $\delta^{18}O$ composition of all calcite cements are similar (about -5) despite the fact that they were formed at different temperatures. This suggests that cementation occurred in a closed system. The $\delta^{18}O$ composition of the

pore water that precipitated these calcites evolved systematically to precipitate calcite with $\delta^{18}\text{O}$ composition of -5 at all temperatures.

(5) The $\delta^{13}\text{C}$ composition of post-bitumen calcite cements (ranging from -2 to -17) are depleted relative to that of pre-bitumen ones (ranging from +2 to +5) indicate significant contribution from thermogenic methane in the formation of post-bitumen calcite cements. The $\delta^{13}\text{C}$ composition of calcite that replaces anhydrite (+4 to -2) suggests that carbon used in the formation this calcite was mostly derived from the carbonate host rock.

(6) The strontium isotopic composition of carbonate cements (calcite and dolomite) and allochems are similar to that of Late Jurassic sea water (0.7070) suggesting that no significant radiogenic strontium has entered the system. This also supports the conclusion that cementation occurred in a closed system.

(7) Comparison of the trace element contents of pre- and post-bitumen calcites suggests that during burial the Sr/Ca of pore fluids increased, Mg/Ca decreased, Fe was removed, and Mn/Ca did not vary significantly. Trace element composition of post-bitumen calcite can be reasonably related to precipitation from a pore fluid similar to the present Smackover brine in East Nancy field.

(8) Near total destruction of hydrocarbon gases are due to closed system diagenesis, abundant sulfate, and lack of

metal ions to serve as a sink for the H_2S generated during hydrocarbon destruction.

(9) Intergranular limestone porosity is destroyed by physical and chemical compaction at a burial depth of 19,000 ft (5,795 m). Dolomites however, show sufficient porosity (1-20%) to serve as economic reservoirs at depths of 19,000 ft (5,785 m) or greater.

(10) Point counting results indicate that undolomitized grainstones contain 0% to 16.6% marine cement, 4.7% to 18.5% pre-bitumen calcite cement, 0% to 8.8% saddle dolomite, 0% to 39.6% replacement anhydrite, 0% to 18.4% bitumen pore fill, and 0% to 11.9% post-bitumen calcite cement. The total cement ranges from 5% to 35.3%. The dolomite contain 4.5% to 38.8% bitumen cement, 1.3% to 18.1% post-bitumenc calcite cement, 0% to 2.5% fluorite, and 1.1% to 16.3% thin section porosity.

ACKNOWLEDGEMENTS

This research was supported by the Department of Geology and Applied Carbonate Research Program of Louisiana State University. We thank Phillips Petroleum Company for releasing the cores used in this study; L. S. Land for oxygen and strontium isotope analyses and beneficial discussions; R. Koepnick for providing strontium isotopes of allochems. A critical review by J. S. Hanor significantly improvement the manuscript. R. D. Snelling provided trace

element analyses critical discussions. W. LeBlanc for X-ray diffraction analyses; K. Lyle for photography; and M. Moore, B. Delaville, F. Couvillon, and C. Weber for providing good cheer. B. L. Kirkland and W. J. Wade reviewed the manuscript and made valuable comments. Discussions with R. Sassen were helpful throughout the course of this study and special thank goes to M. L. Machain for her support during this research.

REFERENCES CITED

- Aulsted, K. L., Spencer, R. J., and Krouse, R. H., 1988,
Fluid inclusion evidence on dolomitization, Devonian of
western Canada: *Geochemica et Cosmochemica acta*, v. 52,
p. 1027- 1035.
- Ayalon, A., and Longstaffe, F. J., 1988, Oxygen isotope
studies of diagenesis and pore-water evolution in the
western Canada sedimentary basin: Evidence from the
Upper Cretaceous basal Belly River Sandstone, Alberta:
Journal of Sedimentary Petrology, v. 58, p. 489-505.
- Badon, C. L., 1973, Petrology of the Norphlet and Smackover
Formations (Jurassic), Clarke County, Mississippi:
Unpublished dissertation, Louisiana State University,
197 p.
- 1974, Petrology and reservoir potential of the
upper Smackover Formation, Clarke County Mississippi,
Gulf Coast Association of Geological Societies
Transaction, v. 24, p. 163-174.
- Baker, P. A., Gieskes, J. M., and Elderfield, H., 1982,
Diagenesis of carbonates in deep-sea sediments-evidence
from Sr/Ca ratios and interstitial dissolved Sr^{+2} data:
Journal of Sedimentary Petrology, v. 52, p. 71-82.
- Bathurst, R. G. C., 1980, Deep crystal diagenesis in
limestones: *Revista del Instituto de Investigaciones
Geologicas Dipvtacion Provincial, Universidad de
Barcelona*, v. 34, p. 89-100.

- 1986, Carbonate diagenesis and reservoir development - conservation, destruction and creation of pores: Colorado School of Mines Quarterly, v. 81, p. 1-25.
- Berman, R. G., 1988, Internally-consistent thermodynamic data for minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$: Journal of Petrology, v. 29, p. 445-522.
- Berner, R. A., 1971, Principals of chemical sedimentology: McGraw Hill Book Company, N. y., 240.
- Brand, U. and Veizer, J., 1980, Chemical diagenesis of a multicomponent carbonate system-1: Trace elements: Journal of Sedimentary Petrology, v. 50, p. 1219-1236.
- 1983, Origin of coated grains: Trace element constraints in T. M. Peryt ed., Coated Grains: Springer-Verlag, New York, p. 9-26.
- Buffler, R. T., and Sawyer, D. S., 1985, Distribution of crust and early history of Gulf of Mexico Basin: Gulf Coast Association of Geologic Societies Transactions, v. 35, p. 333-344.
- Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through Phanerozoic time: Geology, v. 10, p. 516-519.
- Carothers, W. W., and Kharaka, Y. K., 1978, Aliphatic acid anions in oil-field waters-implications for origin of

- natural gas: AAPG Bulletin, V. 62, p. 2441-2453.
- Carpenter, A. B., Trout, M. L., and Pickett, E. E., 1974, Preliminary report on the origin and chemical evolution of lead and zinc-rich oil fields brines in central Mississippi: Economic Geology, v. 69, p. 1191- 1206.
- Choquette, P. W., and James, N. P., 1987, Diagenesis #12. Diagenesis in Limestones - 3. The deep burial environment: Geoscience Canada, v. 14, p. 3-35.
- Claypool, G. E., Holser, W. T., Kaplan, I. R., Sakai, H., and Zak, I., 1980, The age curve of sulfur and oxygen isotopes in marine sulfate and their mutual interpretations: Chemical Geology, v. 28, p. 199-260.
- and Mancini, E. A., 1989, Geochemical relationship of petroleum in Mesozoic source rocks of Jurassic Smackover Formation, southwestern Alabama: AAPG Bulletin, v. 73, p. 904-924.
- Clayton, R. N., Friedman, I., Graf, D. L., Mayeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The origin of saline formation waters: Journal of Geophysical Research, v. 71, p. 3869-3882.
- O'Neil, J. R., Mayeda, T. K., 1972, Oxygen isotope exchange between quartz and water: Journal of Geophysical Research, v. 77, p. 3057-3067.
- Davis, J. B., and Kirkland, D. W., 1970, Native sulfur deposition in the Castile Formation, Culberson County, Texas: Economic Geology, v. 65, p. 107-121.

- 1979, Bioepigenetic sulfur deposits: *Economic Geology*, v. 74, p. 462-468.
- Dickson, J. A. D., 1966, Carbonate identification and genesis as revealed by staining: *Journal of Sedimentary Petrology*, v. 36, p. 491-505.
- and Coleman, M. L., 1980, Changes in carbon and oxygen isotope composition during limestone diagenesis: *Sedimentology*, v. 27, p. 107-118.
- Dinkins, T. H., 1967, Jurassic stratigraphy of central and southern Mississippi: *Mississippi Geological Survey Bulletin*, v. 109, p. 9-37.
- Dixon, S. A., Summers, D. M., and Surdam, R. C., 1989, Diagenesis and preservation of porosity in Norphlet Formation (Upper Jurassic), southern Alabama: *AAPG Bulletin*, v. 73, p. 707-728.
- Drean, T. A., 1978, Reduction of sulfate by methane, xylene, and iron at temperatures of 175 to 350 °C. M.S. Thesis, the Pennsylvania state University, 90 p.
- Dutton, S. P., and Land, L. S., 1988, Cementation and burial history of a low-permeability quartz arenite, Lower Cretaceous Travis Peak Formation, East Texas: *GSA Bulletin*, v. 100, p. 1271-1282.
- Eldridge, J. T., 1989, Upper Jurassic stratigraphy, porosity distribution, and hydrocarbon potential of western southern Mississippi: Unpublished M. S. Thesis, Louisiana State University, 179 p.

- Fanelli, R., 1949, Solubility of hydrogen sulfide in sulfur: Industrial and Engineering Chemistry, v. 41, p. 2031-2033.
- Farmer, R. E., 1965, Genesis of subsurface carbon dioxide: AAPG Memoir 4, p. 378-385.
- Feazel, C. T., 1985, Diagenesis of Jurassic grainstone reservoirs in the Smackover Formation, Chatom field, Alabama, in P. O. Roehl, and P. W. Choquette, eds., Carbonate petroleum reservoirs: Springer-Verlag, New York, p. 357-367.
- Fisher, A. G., and Arthur, M. A., 1977, Secular variation in the pelagic realm, in, H. Cook, and P. Enos, eds., Deep-water carbonate environments: SEPM, Special Publication 25, p. 19-50.
- Fuchtbauer, H., and Hardie, L. A., 1976, Experimentally determined homogeneous distribution coefficients for precipitated magnesian calcite: Abstract Annual Program Meeting, Geological Society of America, v. 8, p. 877.
- Grizzaffi, L. P., and Thompson, B. M., 1970, Completing gas wells that produce high H₂S: World Oil, #7, p.70-74.
- Halley, R. B., 1984, Post-depositional diagenesis of metastable carbonates: an overview: Paleontographica Americana, no. 54, p. 245-253.
- 1985, Burial diagenesis of carbonate rocks: Colorado School of Mines, Quarterly, v. 82, p. 1-15.
- 1985, Setting and geologic summary of the

- Lower Cretaceous, Sunniland field, southern Florida, in P. O. Roehl, and P. W. Choquette, eds., Carbonate petroleum reservoirs: Springer-Verlag, New York, p. 443-454.
- Hancock, J. M. and Scholle, P. A., 1975, Chalk of the North Sea, in A. W. Woodland, ed., Petroleum and the Continental Shelf of North-West Europe, v. 1: New York, Wiley and Sons, p. 413-425.
- Hanor, J. S., 1979, The sedimentary genesis of hydrothermal fluids, in H. L. Barnes ed., Geochemistry of hydrothermal ore deposits, second edition: New York, John Wiley and sons, p. 137-174.
- 1986, Distribution of dissolved fatty acids in some Louisiana oil field brines: Applied Geochemistry, v. 1, p. 37-46.
- Helgeson, H. C., Delany, J. M., Nesbitt, H. W., and Bird, D. K., Summary and critique of the thermodynamic properties of rock-forming minerals: American Journal of Science, v. 278-A, p. 1-229.
- Heydari, E., Moore, C. H., and Sassen, R., 1988, Late burial diagenesis driven by thermal degradation of hydrocarbons and thermochemical sulfate reduction: Upper Smackover carbonates, southeast Mississippi, AAPG Bulletin, v. 72, p. 197.
- 1989, Post-hydrocarbon migration deep burial diagenesis of the Smackover Formation,

- Black Creek field, Mississippi salt basin, AAPG Bulletin, v. 73, p. 363.
- 1989, Burial diagenesis and thermochemical sulfate reduction, Smackover Formation, southeast Mississippi salt basin: Geology, v. 17, p. 1080-1084.
- Houseknecht, D. W., 1987, Assessing the relative importance of compaction processes and cementation to reduction of porosity in sandstones, AAPG Bulletin, v. 71, p. 633-642.
- Hovland, M., Talbot, R. M., Qvale, H., Olausson, S., and Aasberg, L., 1987, Methane-related carbonate cements in pockmarks of the North Sea: Journal of Sedimentary Petrology, v. 57, p. 881-892.
- Hyne, J. B., 1983, Controlling sulfur deposition in sour gas wells: World Oil, August, p. 35-46.
- and Derdall, G. D., 1980, How to handle sulfur deposition by sour gas: World Oil, October, p. 111-120.
- Imlay, R. W., 1980, Jurassic Paleobiography of the conterminous United State in its continental setting: USGS Professional Paper 1062, 134 p.
- Katz, A., 1973, The interaction of magnesium of with calcite during crystal growth at 25-90 °C and one atmosphere: Geochemica et Cosmochemica Acta, v. 37, p. 1563-1586.
- , Sass, E., Starinsky, A., 1972, Strontium behaviour in the aragonite-calcite transformation: an

- experimental study at 40-90 °C: *Geochemica et Cosmochemica Acta*, v. 36, p. 481-440.
- Kehle, R. O., 1971, Geothermal survey of North America, 1971 annual progress report: Unpublished duplicate report, research committee, AAPG, Tulsa, OK, 31p.
- Kharaka, Y. K., Maest, A. S., Carothers, W. W., Law, L. M., Lamothe, P. J., and Fries, T. L., 1987, Geochemistry of metal-rich brine from central Mississippi: *Applied Geochemistry*, v. 2, p. 543-561.
- Kinsman, D. J. J., 1969, Interpretation of Sr^{++} concentration in carbonate minerals and rocks: *Journal of Sedimentary Petrology*, v. 39, p. 486-508.
- Kirkland, D. W., and Evans, R., 1976, Origin of limestone buttes, Gypsum Plain, Culberson County, Texas, *AAPG Bulletin*, v. 68, p. 2005-2018.
- Knauth, L. P., 1979, A model for the origin of chert in limestone: *Geology*, v. 7, p. 274-277.
- Krouse, H. R., 1980, Stable isotope geochemistry of non-hydrocarbon constituents of natural gas: 10th World Petroleum Congress, p. 85-92.
- Viau, C. A., Eliuk, L. S., Ueda, A., and Halas, S., 1988, Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs: *Nature*, v. 333, p. 415-419.
- Land, L. S., 1979, Chert-chalk diagenesis: the Miocene

- Island Slope of north Jamaica: Journal of Sedimentary Petrology, v. 49, p. 223-232.
- 1980 The isotopic and trace element geochemistry of dolomite: the state of the art, in D. H. Zenger, J. B. Dunham, and R. L. Ethington, eds., Concept and models of dolomitization: SEPM Special Publication 28, p. 87-110.
- 1983, Application of stable isotopes to studies of the origin of dolomite and to problems of diagenesis of clastic sediments, In M. A. Arthur, ed., Stable isotopes in sedimentary geology: SEPM Short Course 10, p. 4-1 - 4-22.
- Behrens, E. W., and Frishman, S. A., 1979, The ooids of Baffin Bay Texas: Journal of Sedimentary Petrology. v. 49, p. 1269-1278.
- and Prezbindowski, D. R., 1981, The origin and evolution of saline formation water, lower Cretaceous carbonates, south-central Texas, U.S.A.: Journal of Hydrology, v. 54, p. 51-74.
- Long, M., 1978, Key areas to determine Jurassic trend's future: Oil and Gas Journal, v. 76 (May 8), p. 117-121.
- Lorens, R. B., 1981, Sr, Cd, Mn, and Co distribution coefficients in calcite as a function of calcite precipitation rate: Geochimica et Cosmochimica Acta, v. 45, p. 553-561

- Matter, A., Douglas, R. G., and Perch-Nielson, K., 1975, Fossil preservation, geochemistry, and diagenesis of pelagic carbonates from Shatsky Rise, northwest Pacific: Initial Reports Deep Sea Drilling Project, v. 32, p. 891-921.
- Macqueen, R. W., and Powell, T. G., 1983, Organic geochemistry of the Pine Point lead-zinc ore field and region, Northwest Territories, Canada: Economic Geology, v. 78, p. 1-25.
- McLimans, R. K., (1987), The application of fluid inclusions to migration of oil and diagenesis in petroleum reservoirs: Applied Geochemistry, v. 2, p. 585-603.
- Meendsen, F. C., Moore, C. H., Heydari, E., and Sassen, R., 1987, Upper Jurassic depositional system and hydrocarbon potential of southern Mississippi: Gulf Coast Association of Geological Societies Transactions, v. 37, p. 161-174.
- Moore, C. H., 1984, The upper Smackover of the Gulf rim: Depositional system, diagenesis, porosity evolution and hydrocarbon production in W. P. S. Ventress, D. G. Bebout, B. F. Perkins, and C. H. Moore, eds, The Jurassic of the Gulf rim: Gulf Coast Section SEPM Third annual Research Conference Proceedings, Baton Rouge, Louisiana, p. 283-307.
- 1985, Upper Jurassic subsurface cement - a case history, in N. Schneidermann, and P. M. Harris,

- eds., Carbonate cements: SEPM Special Publication 36, p. 291-308.
- , 1989, Carbonate diagenesis and porosity: Elsevier, New York, 338 p.
- and Druckman, Y., 1981, Burial diagenesis and porosity evolution, Upper Jurassic Smackover, Arkansas and Louisiana: AAPG Bulletin, v. 65, p. 597-628.
- Morrow, D. W., and Meyers, I. R., 1978, Simulation of limestone diagenesis- a model based on strontium depletion: Canadian Journal of Earth Sciences, v. 15, p. 376-396.
- Mucci, A., and Morse, J. M., 1983, The incorporation of Mg^{2+} and Sr^{2+} into calcite overgrowths: Influence of growth rate and solution composition: Geochemica et Cosmochemica Acta, v. 47, p. 217-233.
- Macknight, W. J., and Tobolsky, A. V., 1965, Properties of polymeric sulfur, in B. Meyer, ed., Elemental sulfur chemistry and physics: New York, John Wiley and Sons, p. 95-107.
- Manus, R. W., and Coogan, A. H., 1974, Bulk volume reduction and pressure-solution derived cements: Journal of Sedimentary Petrology, v. 44, p. 466-471.
- Mitra, S., and Beard, W. C., 1980, Theoretical model of porosity reduction by pressure solution for well-sorted sandstones: Journal of Sedimentary Petrology, v. 50, p. 1347-1360.

- Oxley, M. L., Minihan, E., and Ridgeway, J. M., 1968, A study of the Jurassic sediments in portions of Mississippi and Alabama: Gulf Coast Associations of Geological Societies Transactions, v. 17, p. 24-48.
- O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969, Oxygen isotope fractionation in divalent metal carbonates: Journal of chemistry and physics, v. 51, p. 5547-5558.
- Orr, W. L., 1974 Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-study of Big Horn Paleozoic oils: AAPG Bulletin, v. 58, p. 2295-2318.
- 1977, Geologic and geochemical controls on the distribution of hydrogen sulfides in natural gas, in R. Campos, and J. Goni, eds.: Advances in organic geochemistry (1975): Madrid, Emperesa Nacional Adaro de Investigaciones Mineras, v. 7, p. 571-597.
- 1982, Rate and mechanism of non-microbial sulfate reduction: Geological Society of America Abstracts with Program, v. 14, p. 580.
- Parker, C. A., 1974, Geopressures and secondary porosity in the deep Smackover of Mississippi: Gulf Coast Association of Geological Societies Transaction, v. 24, p. 69-80.
- Pierre, C., and Rouch, J. M., 1988, Carbonate replacement after sulfates in the Middle Miocene of Egypt: Journal

- of Sedimentary Petrology, v. 58, p. 446-456.
- Pingitore, Jr, N. E., 1978, The behavior of Zn^{++} and Mn^{++} during carbonate diagenesis: theory and applications: Journal of Sedimentary Petrology, v. 48, p. 799-814.
- and Eastman, M. P., 1986, The coprecipitation of Sr^{++} with calcite at 25 °C and 1 atm: *Geochemica et Cosmochemica Acta*, v. 50, p. 2195-2203.
- Prezbindowski, D. R., 1985, Burial cementation-is it important? A case study, Stuart City trend, south central Texas, in N. Schneidermann, and P. M. Harris, eds., Carbonate Cements: SEPM Special Publication 36, p. 241-264.
- Pryor, W. A., 1962, Mechanism of sulfur reactions: McGraw Hill book inc., N.Y. 241 p.
- Powell, T. G., and Macqueen, R. W., 1984, Precipitation of sulfide ores and organic matter: Sulfate reactions at Pine Point, Canada: *Science*, v. 224- p. 63-66.
- Price, N. J., 1975, Fluids in the crust of the Earth: *Scientific Progress*, v. 62, p. 59-87.
- Richardson, C. K., and Holland, H. D., 1979a, Fluorite deposition in hydrothermal systems: *Geochemica et Cosmochemica Acta*, v. 43, p. 1327-1335.
- 1979b, Solubility of fluorite in hydrothermal solutions, an experimental study: *Geochemica et Cosmochemica Acta*, v. 43, p. 1313-

1325.

----- and Pinckney, D. M., 1984, The chemical and thermal evolution of the fluids in Cave-in-Rock fluorspar district, Illinois: Mineralogy, Paragenesis, and fluid inclusions: Economic Geology, v. 79, p. 1833-1858.

Rittenhouse, G., 1971, Pore space reduction by solution and cementation AAPG Bulletin, v. 55, p. 80-91.

Rogers, M. A., McAlary, J. M., and Bailey, N. J. L., 1974, Significance of reservoir bitumen to thermal-maturation studies, Western Canada basin: AAPG Bulletin, v. 58, p. 1906-1824.

Saller, A. H., and Moore, B. R., 1986, Dolomitization in the Smackover Formation, Escambia County, Alabama: Gulf Coast Association of Geological Societies Transactions, v. 36, 275-282.

Sassen, R., 1980, Biodegradation of crude oil and mineral deposition in a shallow Gulf Coast salt dome: Organic Geochemistry, v. 2, p. 153-166.

----- 1988, Geochemical and carbon isotopic studies of crude oil destruction, bitumen precipitation, and sulfate reduction in the deep Smackover Formation: Organic Geochemistry, v. 12, p. 352-361.

----- Nunn, J. A., Meendsen, F. C., and Heydari, E., 1987, Geochemical studies of crude oil generation, migration, and destruction in the

Mississippi Salt Basin: Gulf Coast Association of Geological Societies Transaction, v. 37, p. 217-224.

----- and Meendsen, F. C., 1987, Distribution of hydrocarbon source potential in the Jurassic Smackover Formation: Organic Geochemistry, v. 11, p. 379-383.

----- and Moore, F. C., 1988, Framework of hydrocarbon generation and destruction in eastern Smackover trend: AAPG Bulletin, v. 72, p. 649-663.

Schmoker, J. W., and Halley, 1982, R. B., Carbonate porosity versus depth - a predictable relation for south Florida: AAPG Bulletin, v. 66, p. 2561-2570.

Scholle, P. A. and Halley, R. B., 1985, Burial diagenesis - out of sight, out of mind!, in N. Schneidermann, and P. M. Harris, eds., Carbonate Cements: SEPM Special Publication 36, p. 309-334.

Sharma, T., and Clayton, R. N., 1965, Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates: Geochimica et Cosmochimica Acta, v. 29, p. 1347-1353.

Sheppard, S. M. F., 1986, Characterization and isotopic variations in natural waters, in J. W. Valley, H. P. Taylor, Jr., and J. R. O'Neil, eds., Stable isotopes in high temperature geologic processes: Mineralogical Society of America, Reviews in Mineralogy, v. 16, p. 165-180.

Shock, E. L., Organic acid metastability in sedimentary

brines: *Geology*, v. 16, p.886-890.

- Siebert, R. M., 1985, The origin of hydrogen sulfide, elemental sulfur, carbon dioxide, and nitrogen in reservoirs, in Sixth Annual Research Conference, Gulf Coast Section: SEPM Foundations, Austin, Texas, Dec. 1-4, 1985, p. 30-31.
- Spirakis, C. S., and Heyl, A. V., 1988, Possible effect of thermal degradation of organic matter on carbonate paragenesis and fluorite precipitation in Mississippi Valley-type deposits: *Geology*, v. 16, p. 1117-1120.
- Stoessell, R. K., and Moore, C. H., 1983, Chemical constrains and origins of four groups of Gulf Coast reservoir fluids: *AAPG Bulletin*, v. 67, p. 896-906.
- , Klimentidis, R. E., and Prezbindowski, D. R., 1987, Dedolomitization in Na-Ca-Cl brine from 100 to 200 °C at 300 bars: *Geochemica et Cosmochemica Acta*, v. 51, p. 847- 855.
- Surdam, R. C., Boese, S. W., and Crossey, L. J., 1984, The chemistry of secondary porosity in McDonald, D. A., and Surdam, R. C., eds, *Clastic diagenesis*: AAPG Memoir 37, p. 127-149.
- Swift, S. C., Manning, F. C., Thompson, R. E., 1976, Sulfur-bearing capacity of hydrogen sulfide gas: *Society of Petroleum Engineers Journal*, v. 16, p. 57-64.
- Takach, N. E., Baker, C., and Kemp, M. K., 1987, Stability of natural gas in the deep subsurface: *Thermodynamic*

- calculation of equilibrium composition: AAPG Bulletin, v. 71, p. 322-333.
- Taylor, H. P., Jr., 1977, Water/rock interactions and the origin of H₂O in granitic batholiths: Journal of Geological Society of London, v. 133, p. 509-558.
- Tan, F. C., and Hudson, J. D., 1974, Isotopic studies on the paleoecology and diagenesis of the Great Esturine Series (Jurassic) of Scotland: Scottish Journal of Geology, v. 2, p. 91-128.
- Toland, W. G., 1960, Oxidation of organic compounds with aqueous sulfate: Journal of the American Chemical Society, v. 80, p. 1911-1916.
- Tobolsky, A. V., 1964, Polymeric sulfur and other polysulfide polymers: American Scientist, v. 52, p. 358-364.
- Tuller, W. N., 1954, The sulfur data book, McGraw-Hill Book Company, N. Y., 143p.
- Vinet, M. J., 1984, Geochemistry and origin of Smackover and Buckner dolomites (upper Jurassic), Jay Field area, Alabama-Florida, in W. P. S. Ventress, D. G. Bebout, B. F. Perkins, and C. H. Moore, eds., The Jurassic of the Gulf rim: Gulf Coast Section SEPM Third annual Research Conference Proceedings, Baton Rouge, Louisiana, p. 365-374.
- Voronkov, M. G., Vyazonkin, N. S., Deryagina, E. N., Nakhmanovich, A. S., and Usov, V. A., 1987, Reaction of

- sulfur with organic compounds: Pizey, J. S. ed., Consultants Bureau, N. Y., 241p.
- Wade, W. J., Hanor, J. S., and Sassen, R., 1989, Controls on H₂S concentration and hydrocarbon destruction in the eastern Smackover trend: Gulf Coast Association of Geological Societies Transactions, v. 39, p. 309-320.
- Wakelyn, B. D., 1977, Petrology of the Smackover Formation (Jurassic): Perry and Stone Counties, Mississippi: Gulf Coast Associations of Geological Societies Transactions, v. 27, p. 386-408.
- Wanless, H. R., 1983, Burial diagenesis in limestones, in A. Parker, and B. W. Sellwood, eds., Sediment diagenesis, p. 379-417.
- Waples, D. W., 1980, Time and temperature in petroleum formation: Application of Lopatin's method to petroleum exploration: AAPG Bulletin, v. 64, p. 916-926.
- Wiewiorowski, T. K., and Touro, F. J., 1966, The sulfur-hydrogen sulfide system: Journal of Physical Chemistry, v. 70, p. 234-238.
- Wood, M., and Walper, J. L., 1974, The evolution of the interior Mesozoic Basins and the Gulf of Mexico: Gulf Coast Association of Geological Societies Transactions, v. 24, p. 31-41.
- Workman, A. L., and Hanor, J. S., 1985, Evidence for large scale fatty acids in Louisiana oil field brines: Iberia field, south-central Louisiana: Gulf Coast Association

- of Geological Societies Transaction, v. 35, p. 293-300.
- Woronick, R. E., and Land, L. S., 1985, Late burial diagenesis, Lower Cretaceous Pearsal and lower Glen Rose Formations, south Texas, in N. Schneidermann, and P. M. Harris, eds., Carbonate Cements: SEPM Special Publication 36, p. 265-275.
- Yeh, H. W., and S. M. Savin, 1977, Mechanism of burial metamorphism of argillaceous sediments: 3.0-isotope evidence: Geological Society of America Bulletin, v. 88, p. 1321-1330.
- Zempolich, W. G., B. H. Wilkinson, and K. C. Lohmann, 1988, Diagenesis of Late Paleozoic carbonates: Journal of Sedimentary Petrology, v. 58, p. 656-672.

CHAPTER V

APPENDIX A

ANHYDRITE AND SULFUR DISTRIBUTIONS IN THE

PHILLIPS #1A JOSEPHINE

The quantitative distributions of calcite, saddle dolomite, and late diagenetic anhydrite in the upper grainstone portion of the Phillips #1A Josephine and the Phillips #1A Flurry were presented in Table 2, Chapter 4. The remaining section of both wells are composed of packstone, wackestone, and mudstone. No significant information can be gathered from point counting of these rocks. Therefore, concentration of anhydrite was visually estimated from thin sections and cores and shown in Figure A1 for the Josephine well. Anhydrite shows similar distribution in the Flurry well.

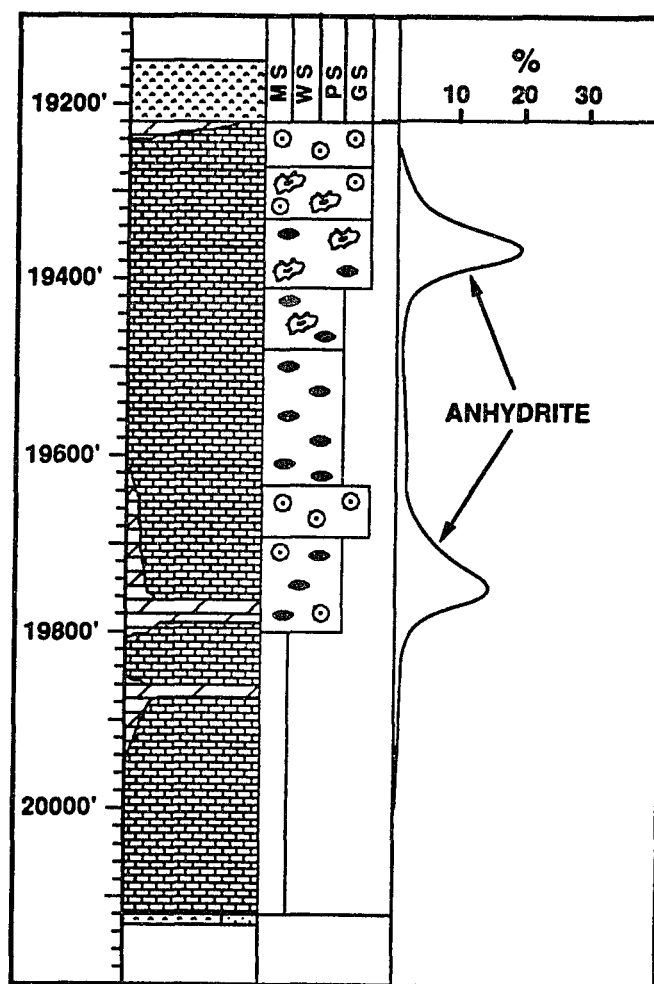
Anhydrite occurs through out both wells but exhibits two intervals of maximum concentration. An upper one at about 19300-19400 ft and a lower one at about 19700-19800 ft. The anhydrite in the upper interval occurs as crystal laths and altered totally to a fine crystalline calcite (Fig. A2). The Anhydrite in the lower part occurs as large nodules or as massive replacement of the Smackover carbonates (Fig. A3). The anhydrite in the lower part is altered to either calcite + elemental sulfur (Fig. , Chapter 4), or elemental sulfur alone (Fig. A4). The reasons for the distributions of anhydrite through out the well is not clear. Neither is the cause for its mode of occurrence (crystal lath in the upper part versus nodules in the lower

part).

Elemental sulfur was not observed in altered anhydrite laths in the upper part of the well. It is possible that it occurs in very small submicroscopic forms which can not be seen or distinguished with a petrographic microscope.




Anhydrite nodules in the lower part of the well have altered to elemental sulfur which is generally present where anhydrite nodules occur.

Figure 5.1. Stratigraphic column of the Phillips #1A Josephine showing estimated distribution of anhydrite throughout the well.







LEGEND

GRAIN TYPES

-  OIDS
-  PELLETS AND PELOIDS
-  ALGALLY COATED GRAINS

LITHOLOGIES

-  LIMESTONE
-  DOLOMITE
-  SANDSTONE
-  ANHYDRITE

GS = GRAINSTONE

MS = MUDSTONE

PS = PACKSTONE

WS = WACKESTONE

Figure 5.2. Photomicrograph of anhydrite laths altered to fine crystalline calcite. Phillips #1A Josephine, 19,370 ft.

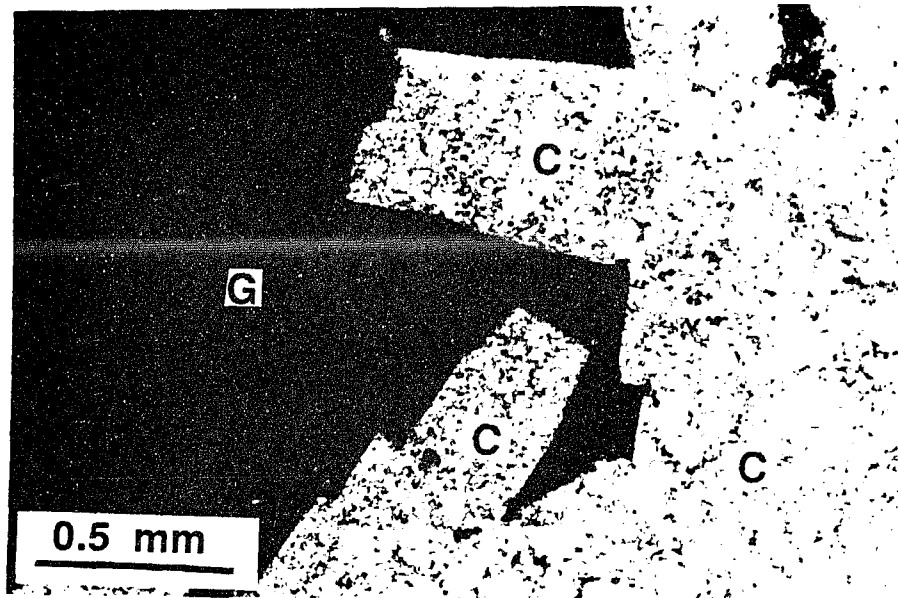


Figure 5.3. Core photograph showing massive replacement of
smackover carbonates by anhydrite. Phillips #1 Flurry, 19744
ft.

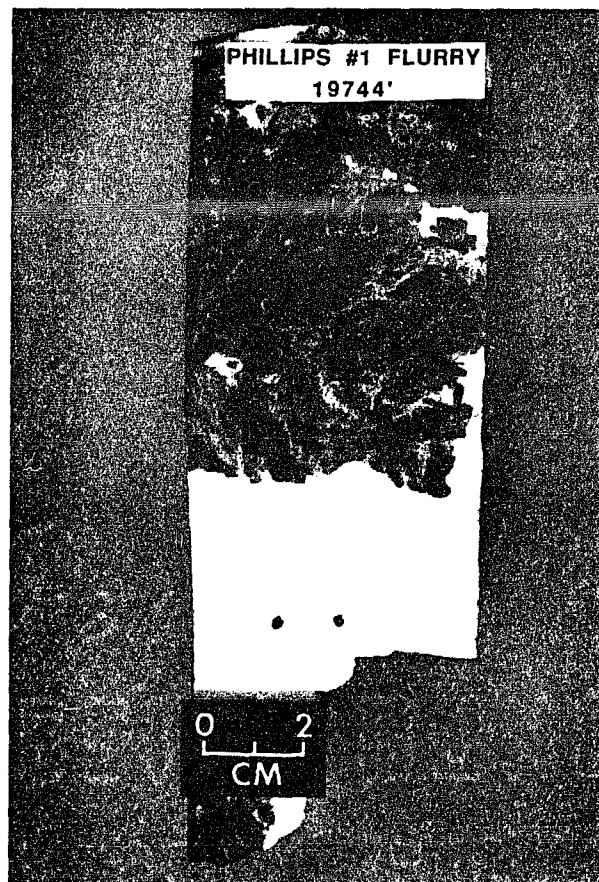
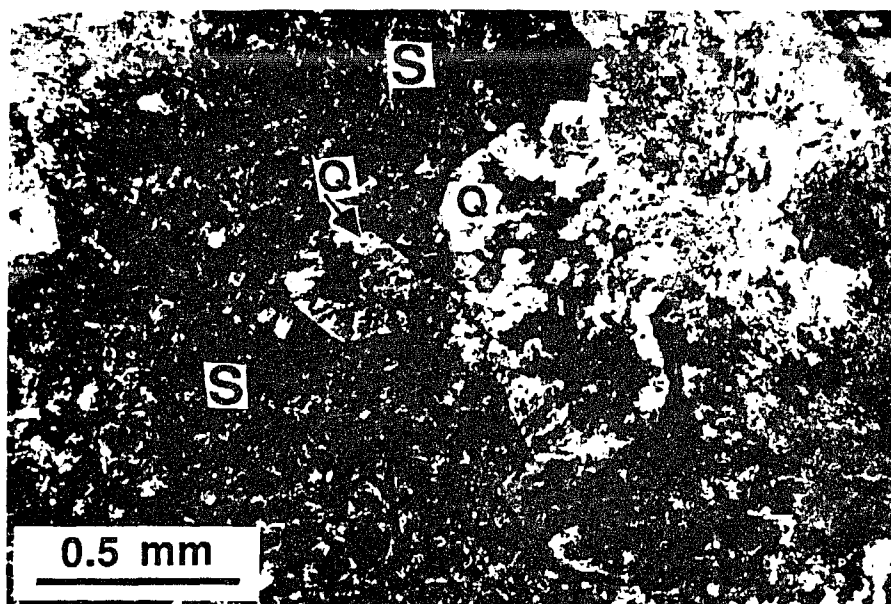


Figure 5.4. Photomicrograph of an anhydrite nodule altered to elemental sulfur (S). Small white elongated laths are remanent anhydrite. Q=late quartz. Phillips #1A Josephine 19578 ft.



VITA

Ezat was born on April 22, 1954, in the village of Laibid, approximately 50 miles southwest of Esfahan in central Iran. He started his education in the village elementary school. The heydari's moved to Ray about 20 miles south of Tehran in 1964. Ezat graduated from Azimiyeh high school in 1972. The same year he was admitted to the University of Tehran. Ezat received his B.S. degree in 1976 with highest distinction from the Department of Geology. Ezat attended Pennsylvania State University in the Spring of 1978 and received his M.S. degree in geology in the Fall of 1981. His master thesis included structural geology and Cenozoic stratigraphy of the Resting Spring Range in the Death Valley region, eastern California. Ezat entered the doctoral program in geology at the Louisiana State University. He is presently a post-doctoral fellow with the Basin Research Institute of the Louisiana State University.

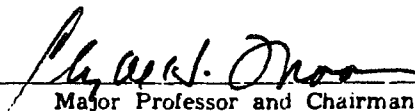
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Ezat Heydari-L

Major Field: Geology

Title of Dissertation: Burial Diagenesis of the Smackover Formation Southeast Mississippi
Salt Basin

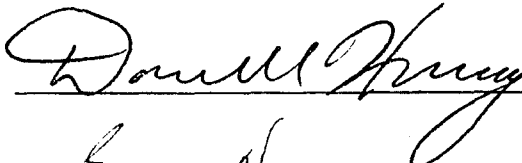
Approved:

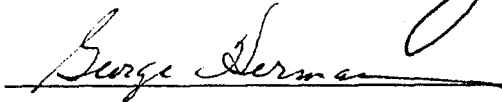

Major Professor and Chairman

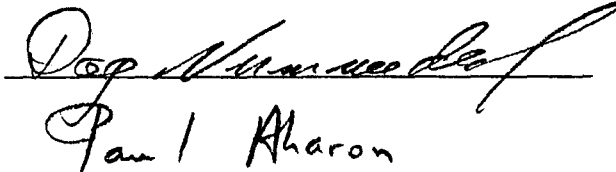

Dean of the Graduate School

EXAMINING COMMITTEE:








Paul Aharon



Date of Examination:

February 13, 1990